

AFIT/GEE/ENV/96D-08

Study of Desorption of Contaminant
from Synthetic Soil

THESIS

Kung-Fu Hwang, Lt. Col., CAF, BSC

AFIT/GEE/ENV/96D-08

DATA QUALITY IMPROVED 3

Approved for public release; distribution unlimited

19970805 030

The views expressed in this thesis are those of the author and do not reflect the official policy or position of the Department of Defense or the U. S. Government

AFIT/GEE/ENV/96D-08

**STUDY OF DESORPTION OF CONTAMINANT
FROM SYNTHETIC SOIL**

THESIS

Lt. Col. Kung-Fu Hwang

**Presented to the Faculty of the Graduate School
of Engineering of the Air Force Institute of Technology**

In Partial Fulfillment of the Requirements

for the Degree

of the Master of Science

in Engineering and Environmental Management

**Edward Heyse, Maj, USAF, BSC
Committee Cochairman**

**David Coulliette, Lt Col, USAF
Committee Cochairman**

**Jeffrey Martin, Maj, USAF
Committee Member**

AFIT/GEE/ENV/96D-08

**STUDY OF DESORPTION OF CONTAMINANT
FROM SYNTHETIC SOIL**

THESIS

Presented to the Faculty of the School of Engineering of the

Air Force Institute of Technology

Air Education and Training Command

In Partial Fulfillment of the Requirements for the Degree of

the Master of Science in Engineering and Environmental

Management

Kung-Fu Hwang

Lt. Colonel, Republic Of China Air Force

December 1996

Approved for public release; distribution unlimited

Acknowledgments

I am very grateful to my thesis advisor, Major Edward Heyse, who has coordinated my courses and carefully guided my progress throughout my master's program. Especially, this research would not have been possible without his direction and patient encouragement of my learning of thesis process.

I would also like to thank my committee members, Lt. Col. David Coulliette and Major Jeff Martin. Lt. Col. Coulliette, together with Major Heyse, developed a computer program for Mass Transfer Models, which successfully allowed me to model my experimental data. Major Martin was invaluable in helping me with instrumentation knowledge.

A special thank-you is given to Dan Mika, who not only guaranteed the analytical instrument ran smoothly, but enlightened me on some discussions of his own findings which aided me considerably in my own research. His company, during the whole experimental and thesis processes, made me feel more comfortable in this intensive research.

Finally, I wish to thank my wife, Hsiu-Fen, and children, Lan and Hao, who sacrificed a lot of quality family time while I was in AFIT program. I especially want to express my thanks to Hsiu-Fen, who took fantastic care of our children primarily by herself so as not to distract me from studying. Her support and understanding, indeed, gave me most of the motivation to fulfill the AFIT program.

TABLE OF CONTENTS

ACKNOWLEDGMENTS	page ii
LIST OF TABLES	v
LIST OF FIGURES	vi
ABSTRACT	vii
CHAPTERS	
I. INTRODUCTION.....	1
II. LITERATURE REVIEW.....	3
Introduction.....	3
Sorption and Desorption Processes.....	3
Sorption Mass Transfer Theories.....	4
Impact of SOM Distribution and Structure on Diffusion Domain.....	5
Diffusion Models for Limited Rate Sorption.....	6
First-Order Approximation and Spherical Diffusion Models.....	6
Multiple Sites in Series Model (MSS).....	8
Synthetic Media.....	11
III. METHODOLOGY.....	14
Materials.....	14
Instrument and Control.....	14
Methods.....	15

Preparing Paraffin with Anthracene.....	15
Making Spheres.....	16
Isotherms.....	17
Desorption Rate Experiments.....	17
IV. DATA DESCRIPTION AND ANALYSIS.....	21
Estimates of Initial Concentration in Wax.....	21
Estimate of Isotherm.....	23
Diffusion Coefficient.....	25
Sorption Capacity Distribution.....	30
V. CONCLUSIONS AND RECOMMENDATIONS.....	34
GLOSSARY.....	36
APPENDICES.....	37
A. HPLC Calibration Curve.....	37
B. Control Analysis of Controls	39
C. Input Files and Codes Used in MSS Model.....	42
REFERENCES.....	107
VITA.....	110

LIST OF TABLES

TABLES	PAGE
1: Number of vials used in each desorption rate experiment.....	18
2 : Summary data prepared for the desorption rate studies.....	19
3: Estimates of initial concentration of anthracene in paraffin compared to heating Time.....	21
4: Initial concentration of anthracene in wax from fitting individual rate experiment data.....	22
5: Summary of fitted diffusion coefficient.....	27
6: ANOVA analysis of effective diffusion coefficient.....	27
7: Estimates of effective diffusion coefficients from sorption and desorption experiments.....	29
8: Summary of fitted geometry parameters.....	30

LIST OF FIGURES

FIGURES	PAGE
1. Frequency distributions of sorption capacity along diffusion path length.....	9
2: MSS conceptual model.....	10
3: Desorption and sorption isotherms.....	24
4: Fitted D_{eff} for individual uniform-sized experiments.....	26
5: Effective diffusion coefficients from sorption and desorption experiments.....	28
6: Fitted and true sorption capacity distribution for evenly mixed experiments.....	32
7: Fitted and true sorption capacity distribution for non-evenly mixed experiments.....	33

ABSTRACT

A better understanding of sorption and desorption processes could improve estimates of time and cost required for remedial activities, exposure times and health risk, and bioavailability. Conventional rate-limited sorption models do not accurately define the diffusion domain at the grain scale. Heyse (1994) proposed the multiple sites in series (MSS) model, which allows more general description of the geometry of the sorption domain than the classical spherical or discrete distributions. A version of this model was tested by deVenoge (1996). The model was able to accurately simulate sorption rate data, but could not estimate unique geometry parameters.

This research is to develop techniques to study desorption, and compare the results to the sorption study conducted by deVenoge (1996). This study examines whether sorption and desorption of anthracene by paraffin are reversible processes. The ability of the MSS model to predict geometry parameters was also tested.

One finding of this study was the apparent volatilization of anthracene from wax during the heating and molding processes. This phenomenon may be responsible for the non-zero intercept of the desorption isotherm. It may have also confounded the initial conditions required by the MSS model in predicting the sorption distribution.

If the initial concentration of anthracene in the wax is adjusted, the desorption process does appear to be the reverse of the sorption process. The equilibrium partition coefficients for sorption and desorption are similar. The diffusion coefficient appears to be faster for desorption than sorption, but this may have been affected by solvation of the paraffin. The MSS model did not successfully predict geometry parameters, possibly due to uncertain initial concentration in wax.

I. INTRODUCTION

Overview of Research Interest:

Contaminated groundwater on Air Force bases, caused primarily by aircraft fuels and solvents released in the past operations, is a major health concern today because many of those hydrophobic chemicals are observed to persist in the environment. After they are sorbed in the sediment and soil systems, their desorption rate is often very slow, with an estimated half life on the order of months to many years (Pignatello, 1990; Pavlostathis and Jaglal, 1991). A better understanding of slow rate-limited desorption behavior is important because it affects exposure time, health risk, time required for remedial activities, clean up costs, and bioavailability (Scow and Alexander, 1992).

Researchers have attributed nonequilibrium of contaminants between water and soil (or sediment) to diffusion (Brusseau et al., 1989a). Understanding the sorption mass transfer process requires a study of sorption / desorption kinetics and the diffusion domain geometry (distribution of sorption capacity along a diffusion path).

In mass transfer modeling, sorption and desorption are generally assumed reversible. However, desorption hysteresis is found in some soils due to their condensed soil organic matter (SOM) matrices (Weber et al., 1996). Conventional desorption processes are measured using batch-reactor decant-refill methods (Bowman, 1979; Weber et al., 1996). Such method exhibits difficulty measuring totally reversible desorption due to the incomplete removal of the liquid phase. Conducting a desorption experiment without a sorption experiment creates difficulties in measuring the initial concentration in the solid phase.

Sorption kinetics generally are modeled using the local equilibrium assumption (LEA), first-order approximations, second-order (diffusion) models, or the combination of these three models. First-order models are normally unable to predict long term tailing (slow desorption process). Diffusion models are mathematically complex and generally limited by assuming only homogeneous particles whose geometry is determined *a priori* (usually spherical). An improved diffusion model proposed by Heyse (1994) is used in this research that allows a more general description of average sorbent particle geometry.

This experimental research focuses on three objectives: (1) to develop techniques to study desorption using synthetic sorbents, (2) to compare sorption and desorption processes in a paraffin / 50:50 methanol and water / anthracene system, and (3) to attempt to predict average particle geometry from desorption batch rate data.

II. LITERATURE REVIEW

Introduction

In this chapter, the literature of the following subjects will be reviewed : (1) the kinetics of sorption and desorption processes, (2) review of conventional diffusion models and the advantages of using multiple sites in series (MSS) model, and (3) previous use of synthetic media, and the advantages and results of using paraffin as synthetic soil in validation of mass transfer models.

Sorption and Desorption Processes

Sorption is a generic term used to describe partitioning of chemicals from a dissolved aqueous phase into sorbent materials and adsorption on mineral surfaces. Desorption describes the reverse process; partitioning and desorption from contaminated solid materials to the aqueous phase. The sorption-desorption characteristics of hydrophobic organic chemicals (HOCs) play an important role in their fate and transport.

Based on Schnitzer's (1978) observation, SOM is largely comprised of humic molecules to include both polar and nonpolar functional groups. SOM has a relatively open and flexible three dimensional polymer-like structure; long bunched chain molecules create intermolecular voids so that HOCs can travel by diffusion in or out of the void spaces, where they associate with the nonpolar functional groups by van der Waals forces. Since the mechanisms of sorption and desorption processes are deemed as the same and reversible, discussion of sorption processes also describes desorption processes.

Sorption Mass Transfer Theories

Some researchers (Di Toro and Horzempa, 1982; Karickhoff and Morris, 1985) provide evidence that sorbed HOCs often display biphasic desorption kinetics from soils and sediments. A labile component of the compound desorbs readily and reversibly, while a resistant component desorbs orders of magnitude more slowly. This phenomena has been observed with polychlorinated biphenyls in both spiked and environmentally contaminated sediments. The slow desorption step has been attributed to the diffusion into microscale sediment particle pores and into SOM (Ball and Roberts, 1991; Pedit and Miller, 1994).

Two theories, based on the distribution of SOM in the soil, describe rate limited sorption process. They are intraorganic matter diffusion (IOMD) and retarded intraparticle diffusion (RIPD). IOMD theorizes that void spaces in the humic polymer-like molecules of SOM are filled with immobile water and HOC solutes from the mobile bulk fluid will diffuse along narrow and tortuous paths into the interior of the SOM to associate with the nonpolar moieties (Karickhoff and Morris, 1985; Brusseau and Rao, 1989b; Nkedi-Kizza et al., 1989; Brusseau et al., 1991). The RIPD theory attributes rate limitations to HOCs diffusing into mineral micropores that are filled with water and are partially or completely filled with SOM (Wu and Gschwend, 1986; Weber and Miller, 1988; Ball and Roberts, 1991; Harmon et al., 1992). IOMD would seem to better describe the nonequilibrium sorption process for those soils with abundant SOM; however, RIPD might do a better job in describing rate-limited sorption for soils with less SOM and high microporosity (Augustijn, 1993).

Impact of SOM Distribution and Structure on Diffusion Domain

To understand diffusion mass transfer processes, a knowledge of diffusion domain (distribution of sorption capacity along a diffusion path), polymer-like structure of SOM (SOM's density), and soil diagenetic history is needed. Soil is normally not comprised of uniform spheres, but exists in a wide range of shapes and sizes. The distributions of SOM in soil are not homogeneous, but exist as discrete particles, coatings on mineral grains (Karickhoff and Morris, 1985; Lion et al., 1990; Barber et al., 1992), or inside mineral micropores (Wu and Gschwend, 1986; Harmon et al., 1992; Ball and Roberts, 1991). In most soils, SOM may be present in all these three categories, and the diffusion process is dominated by the one that is the most abundant. Since SOM may have different diagenetic histories, both sorption capacity and diffusion coefficient of solute can vary with SOM particles. All these factors combine to suggest that the average geometry (relative sorption capacity along a diffusion path at a uniform diffusion coefficient) is probably not spherical. A more likely geometry may be a relatively large capacity near the sorbent / water interface, with smaller capacity at long diffusion path lengths.

The polymer-like structure is identified in two kinds, a condensed glassy inflexible structure or a rubbery flexible structure. The rubbery flexible structure normally implies lower partitioning coefficient (K_p) and higher effective diffusion coefficient (D_{eff}); therefore, HOCs diffuse more easily and faster in and out of the rubbery flexible structure. Linear isotherms and reversible processes for sorption and desorption are appropriate for "flexible" SOM (Pignatello and Xing, 1996; Weber et al. 1996). Condensed, glassy, inflexible structure is characterized by higher K_p and lower D_{eff} . Desorption hysteresis is

often associated with the condensed structure. Isotherm linearity can be restored by conversion of the glassy state to the rubbery state, by increasing the temperature above glass transition point or by softening with organic solvents.

Weber et al. (1996) studied sorption of phenanthrene by ten natural sorbents having different diagenetic histories. The authors found that desorption hysteresis is commonly observed in soils and sediments depending on their diagenetic history. The longer diagenetic history a soil has, the more reduced and condensed the SOM. They also state that the longer diagenetic history of a soil has, the greater will be the sorption capacity, isotherm nonlinearity, and desorption hysteresis.

The higher concentrations of solute diffusing into condensed SOM can increase the diffusion coefficient and the sorption rate. However, pores of the condensed SOM matrices generated by stretching beyond the elastic limit are likely irregularly shaped and may even have no opening after solute is sorbed. Therefore, desorption hysteresis appears to result from microscopic heterogeneities in the diffusion domain.

Diffusion Models for Limited Rate Sorption

First-Order Approximation and Spherical Diffusion Models

Sorption kinetics are modeled using the local equilibrium assumption (LEA), first-order approximations, second-order (diffusion) models, and combinations of these three models. Two common approaches are the two-site model and spherical diffusion model. The two-site model is a combination of an LEA and first-order model that effectively describes the geometry of the sorption domain as a discrete distribution (Karickhoff and Morris, 1985; Brusseau and Rao, 1989b; Ball and Roberts, 1991). The two-site model divides sorption into fast and slow sites. The fast sites are often modeled at equilibrium

with the aqueous phase; the slow sites are modeled with a first-order relationship. Its mathematical description is shown by equations (1) through (3):

$$S = S_1 + S_2 \quad (1)$$

$$S_1 = FK_p C_w \quad (2)$$

$$\frac{dS_2}{dt} = k_2 [K_p C_w (1 - F) - S_2] \quad (3)$$

where S_1 and S_2 are the sorbed concentrations in fast and slow sites; K_p is equilibrium partition coefficient; F is the fraction of fast or equilibrium sites, and k_2 is the mass transfer rate constant.

The development of spherical diffusion model is based Fick's second law. The model equation is described by equation (4):

$$\frac{\partial C}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right) \quad (4)$$

where r is radius of sphere.

This model describes the geometry of sorption domain as uniform spheres. The spherical diffusion model is generally better than the two-site model. The two-site model limits diffusion to linear concentration gradients, but the spherical diffusion model can allow non-linear concentration gradients, which better describe the long term tailing phenomenon observed in the desorption process. However, the spherical diffusion model is mathematically more complex than the two-site model.

Both models can be interpreted as a description of relative sorption capacity ($f(\delta)$) along diffusion path length, δ . The diffusion path length ranges from 0 at the sorbent / water interface to δ_{\max} at the inner most point of the sorption domain.

The two site model is a discrete distribution (Equation 5):

$$f(0) = F \quad (5a)$$

$$f\left(\sqrt{\frac{D_{eff}}{k_2}}\right) = 1 - F \quad (5b)$$

$$f(\delta) = 0 \quad \left\{ \delta \neq 0, \delta \neq \sqrt{\frac{D_{eff}}{k_2}} \right\} \quad (5c)$$

The two site model sorption capacity distribution is illustrated in Figure 1a. The relative sorption capacity for the spherical diffusion model is described by equation (6):

$$f(\delta) = \frac{3}{a^3} (a - \delta)^2 \quad (6)$$

where a is the radius of the sorbent. The sorption capacity distribution for the spherical model is illustrated in Figure 1b.

Multiple Sites in Series Model (MSS)

In order to better simulate sorption or desorption capacity along diffusion path length, Heyse (1994) proposed a multiple sites in series model (MSS). A conceptual MSS model is presented in figure 2.

MSS model is a large number of compartments in series, designed to give added flexibility over the two-site model. Although adding extra compartments implies a problem of more fitting parameters, a function described by 1 or 2 parameters is used in the MSS model to describe the size of each compartment. Therefore, the MSS model is essentially a finite difference approach to the diffusion model, and allows user to put in any function to describe the relative sorption capacity with diffusion path length.

The MSS model has the capabilities of more accurately describing the diffusion

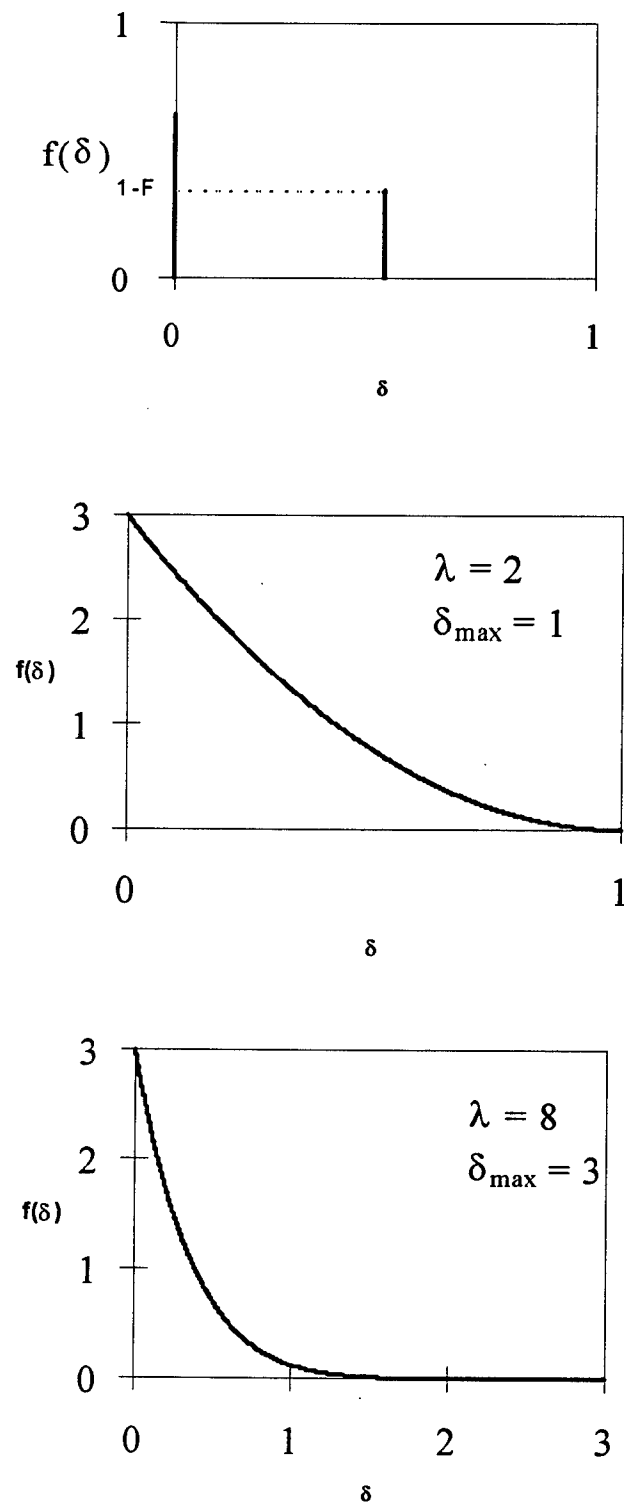


Figure 1. Frequency distributions of sorption capacity along diffusion path length:
a) two-site model; b) spherical model (radius=1); c) MSS model ($\lambda=8$; $\delta_{\max}=3$).

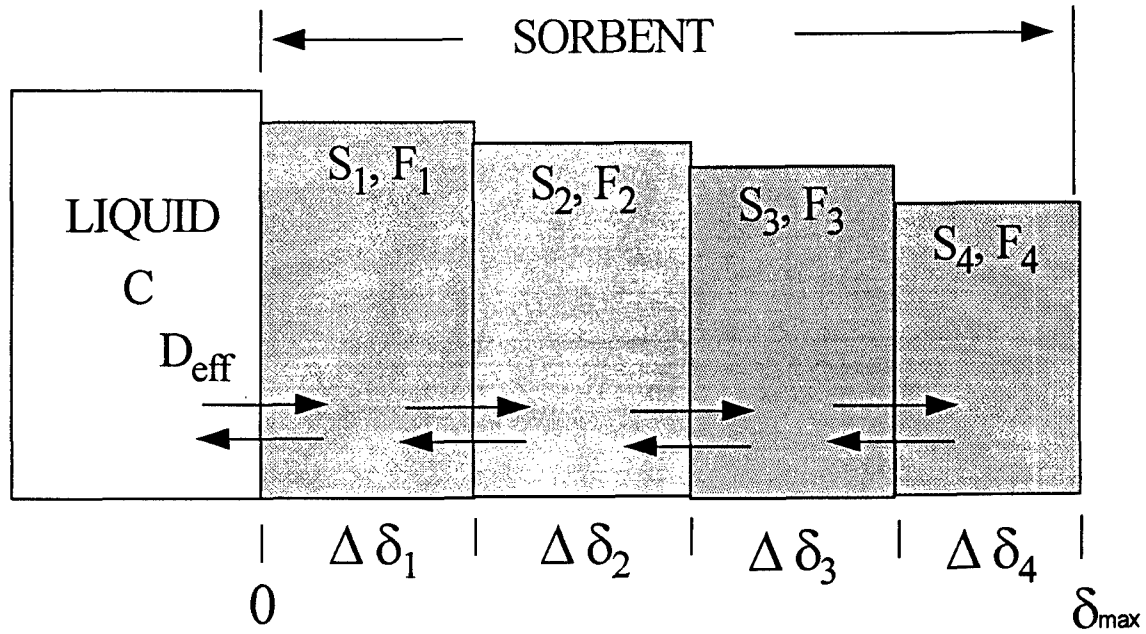


Figure 2: MSS conceptual model (adapted from Heyse, 1994).

process into uniformly sized coatings, spheres, micropores, and variable geometries without adding additional fitting parameters if the partition coefficient, K_p , is determined in advance from batch experiments. Therefore, the MSS model is more likely to be preferable to modeling diffusion processes.

The MSS model describes the changing concentration sorbate in each compartment, $j = 1..n$, by equations (7), (8), and (9).

When $j = 1$:

$$\frac{dS_1}{dt} = -\frac{D_{eff}}{0.5\Delta\delta_1^2} [S_1 - F_1 K_p C] - \frac{D_{eff} F_1}{\Delta\delta_2} \left[\frac{\frac{S_1}{F_1} - \frac{S_2}{F_2}}{0.5(\Delta\delta_1 + \Delta\delta_2)} \right] \quad (7)$$

when $1 < j < n$:

$$\frac{dS_j}{dt} = -\frac{D_{eff} F_j}{\Delta\delta_j} \left[\frac{\frac{S_j}{F_j} - \frac{S_{j-1}}{F_{j-1}}}{0.5(\Delta\delta_j + \Delta\delta_{j-1})} \right] - \frac{D_{eff} F_{j+1}}{\Delta\delta_{j+1}} \left[\frac{\frac{S_j}{F_j} - \frac{S_{j+1}}{F_{j+1}}}{0.5(\Delta\delta_j + \Delta\delta_{j+1})} \right] \quad (8)$$

when $j = n$:

$$\frac{dS_n}{dt} = -\frac{D_{eff} F_n}{\Delta\delta_n} \left[\frac{\frac{S_n}{F_n} - \frac{S_{n-1}}{F_{n-1}}}{0.5(\Delta\delta_n + \Delta\delta_{n-1})} \right] \quad (9)$$

where F is fraction of sorption sites and described by equation (10):

$$F_j = \int_{\sum_{j-1} \Delta\delta_j}^{\sum_j \Delta\delta_j} f(\delta) d\delta \quad (10)$$

deVenoge (1996), Mika (1996), and this research use the function described by equation (11) in the MSS model.

$$f(\delta) = \frac{\lambda + 1}{\delta_{max}^{\lambda+1}} (\delta_{max} - \delta)^\lambda \quad \{ \delta_{max} \geq \delta \geq 0 \} \quad (11)$$

where λ is a shape factor. Classical shapes such as uniform coatings are described when λ equals 0; cylinders when λ equals 1; spheres when λ equals 2. Of interest to this research are geometries where $\lambda > 2$, which display characteristics that may be characteristic of soil sorption capacity. The frequency distribution of sorption sites for this model with diffusion path length is illustrated in figure (1c).

Synthetic Media

Since the diffusion domain is not known in real soil and sediment systems, synthetic media with known sorbent geometries have been used to validate rate-limited

sorption models. Synthetic media used by researchers include: paraffin (Heyse, 1994; deVenoge, 1996), nylon (Heyse, 1994; Mika, 1996), ceramic spherical aggregates (Rao et al., 1980; Skow and Alexander, 1992; Mika, 1996), and synthetic humic-clay complexes (Rebhum et al., 1992).

Some advantages of using paraffin as a SOM surrogate are noted: (1) paraffin is easily melted and molded into desired geometries such as spheres or coatings; (2) the solute of interest can be dissolved into molten paraffin, and used for desorption studies with known, uniform initial concentration in the sorbed phases; (3) the sorption process of anthracene in paraffin appears to be a diffusion-limited partitioning process (Heyse 1994).

Heyse (1994) conducted sorption and desorption experiments in a continuously stirred flow reactor using household paraffin. He was unable to predict consistent diffusion parameters from his experiments. Heyse surmised his results were possibly due to (1) failure in making consistent spherical paraffin beads (more like disks) that might result in misjudgment of diffusion path length, or (2) heating during melting/molding made paraffin more hydrophobic.

deVenoge (1996) used a 99% pure paraffin and successfully created spherical paraffin geometries by using a stainless steel plate to mold melted paraffin into cylinders for shaping, and then using several thin gage steel templates to create paraffin spheres of various sizes. deVenoge also developed sorption isotherms for paraffin subjected to different heating times. All of these isotherms were linear and had consistent partition coefficients. This demonstrated that paraffin could be heated to temperatures of up to 100° C for hours without affecting the sorption capacity. deVenoge did note that fitted

sorbent diffusion coefficients were dependent on bead size. One likely cause of this phenomenon is that he did not solvate his beads prior to initiating sorption rate experiments. Further, deVenoge's experiments were able to accurately predict sorbent geometry for a one parameter fit, but solution for two-parameter fits were not unique.

This research will be using the same paraffin and similar methods of making spheres as deVenoge used. Various sizes of spheres will also be made approximately the same as deVenoge's. In this desorption study, the method of determining initial sorbent concentration, C_{s_i} , will be developed; perturbation, a process of alternatively changing initial and boundary conditions, is also introduced in rate experiments. Desorption isotherm and rate data will be compared to deVenoge's sorption isotherm and rate data to investigate if sorption and desorption are totally reversible processes using paraffin as synthetic media. Using the MSS model prediction of geometrical parameters from rate data involving a heterogeneous mix of spheres is attempted.

III. METHODOLOGY

Materials

Anthracene (99% pure) procured from Aldrich Chemical Company was chosen as solute because it is nonpolar and has low volatility. Its nonpolar characteristics make it similar to other contaminants of petroleum hydrocarbons, and its low volatility minimizes mass losses to headspace.

The solvent for these experiments was 50:50 methanol and distilled water. Methanol was used as cosolvent to increase anthracene's solubility. For some experiments, a stock solution was made by dissolving anthracene in the 50:50 methanol and distilled water. The stock solution contained approximately 1.019 $\mu\text{g/ml}$ anthracene.

Paraffin (99% pure) produced by Aldrich Chemical Company was used as synthetic soil. Methanol does not remove many constituents from this paraffin; it provides a very clean chromatogram for our solvent of choice.

Instrument and Control

Samples were analyzed using Hewlett-Packard High Performance Liquid Chromatograph (HPLC) model HP1090 Series L, using a diode array detector. Samples were injected by an autosampler / autoinjector. Injected sample size could vary from 0.1 to 25 μl according to the sensitivity of a sample's concentration, but the usual sample size was 10 μl . The column was an Adsorbosphere analytical column, 150 x 4.6 mm, (Alltech), having a C18 bonded phase and 5 micron packing. The lamp was warmed up at least an hour before sampling; the detector was set to detect the anthracene's maximum absorption wave length, 248 nm with a band width 32 nm. The reference wave length was

450 nm with a band width 200 nm. The HPLC mobile phase was 100% HPLC grade methanol, and the mobile phase velocity was maintain at a constant rate of 1 ml / min.

Since sample analyses results from the HPLC were reported as peak area under a breakthrough curve, five known solute concentrations were used to develop a calibration curve, which was used to convert the reported peak areas under a breakthrough curve analyzed from samples to estimate the solute's concentration. Detailed information regarding the calibration curve is provided in Appendix A.

In order to ensure the HPLC was providing consistent results, a solution of known solute concentration was used as a control. Detailed analysis of control data is provided in Appendix B.

Methods

Preparing Paraffin with Anthracene

A known mass of anthracene was dissolved in known mass of molten paraffin. This provided paraffin that was contaminated with a known concentration of anthracene for desorption experiments. The initial concentration, C_{s_i} , for this experiment was 19.74 $\mu\text{g/g}$.

C_{s_i} was designed based on the experimental requirement for low enough concentration of anthracene in paraffin to give final concentration in solvent of $< 1 \mu\text{g/ml}$. To achieve this requirement, the mass of anthracene to be dissolved in paraffin was fairly small and difficult to weigh. In order to have enough anthracene to have confidence in the measured concentration when weighing, serial dilution was used by first diluting higher mass of anthracene ($\sim 0.01 \text{ g}$) in paraffin ($\sim 20 \text{ g}$), then again diluting a subsample of that

mixture (~ 6 out of 20 g) with more wax (~ 200 g). The serial dilution is described by equations (12) and (13):

$$C_{s_{mixture}} = \frac{Mass_{Anthracene}}{Mass_{Anthracene} + Mass_{Paraffin}} \quad (12)$$

$$C_{s_i} = \frac{Mass_{mixture} C_{s_{mixture}}}{Mass_{mixture} + Mass_{Paraffin}} \quad (13)$$

Paraffin after serial dilution was separated and kept into seven 50 ml beakers. One beaker of paraffin was used after another was depleted to minimize exposure of the anthracene paraffin mixture to heat. However, after large and medium spheres were finished, all paraffin contained in beakers was depleted. Residual paraffin therefore was reused to make small spheres. Lastly, shredded paraffin for batch isotherm was used after small spheres were finished. Therefore, shredded paraffin was subjected to the longer heating time, followed by the smallest spheres, and the wax in the large and medium spheres were heated for the shortest time.

Making Spheres

Different sizes of paraffin spheres were created by using molding and shaping processes. Paraffin was melted at low temperature around 70 °C (just high enough to melt paraffin). A plastic mold was used to create cylinder-like shapes from molten paraffin. Cooled paraffin was extracted from the mold by pushing with a dowel rod. The plastic mold produced cylinders of approximate dimensions 1 cm thick by 0.6 cm diameter.

A thin gauge stainless steel template with three holes of different diameters then was used to turn and shape the partially-molten paraffin into desired spherical beads. The

diameters of the spherical beads were measured as : large bead, 0.594 cm; medium bead, 0.498 cm; and small bead, 0.399 cm.

Isotherms

Batch isotherm experiments were conducted to determine the equilibrium partitioning coefficient, K_p . To speed up the process and determine an effective K_p value, synthetic surrogates are usually pulverized or shredded to shorten diffusion path length (Heyse, 1994; deVenoge, 1996; Mika, 1996; Pignatello, 1996). In this experiment, the paraffin-anthracene mixture was shredded into pieces using a metal net, and different masses of paraffin-anthracene mixture were placed in different 5 ml or 40 ml amber vials, containing approximately 4 ml or 30 ml 50:50 methanol and water respectively. The paraffin-anthracene mixture was assumed to have the same initial concentrations in the solid phase. The solvent phase was analyzed after more than 21 days equilibrium time.

Desorption Rate Experiments

Desorption experiments were conducted in batch mode using 40 ml amber vials; each vial contained approximately 2 g of paraffin spheres and 20 ml of solvent. There were five combinations of shapes in the vials: large (L), medium (M), small (S) spheres, evenly mixed (EM), and not evenly mixed (NEM) with 3 different spherical sizes. Experiments were conducted up to five different ways that boundary conditions were changed throughout the experiment: (1) no perturbation (NP), (2) removing most of the solvent after one-week sampling, then replacing approximately same volume of clean solvent (RMRC), (3) removing most of the solvent after one-week sampling, then replacing approximately same volume of stock solution (RMRS), (4) continuously removing all of the solvent every week, and replacing with approximately 20 ml of clean

solvent (RARC), and (5) removing all of the solvent every week, then alternatively replacing with approximately 20 ml of clean or stock solution (RARCS). The types of experiments are summarized in Table 1. Details on mix of bead sizes in each experiment are given in Table 2.

Table 1: Number of vials used in each desorption rate experiment

Experiment Type	Bead Mix				
	L	M	S	EM	NEM
NP	2	2	2	2	2
RMRC	2	--	--	2	2
RMRS	2	2	2	2	2
RARC	2	2	2	2	2
RARCS	2	--	--	2	2

Solvent was removed and replaced by pipette for RMRC and RMRS experiments. Solvent was removed from RARC and RARCS vials by pouring out all of the solvent and paraffin beads into filter paper. After filtering the solvent, the paraffin beads were then immediately poured back into the vials, and then new solvent was placed in the vials with pipette. The advantage of using filter paper was that solvent could be removed and paraffin beads replaced in each vial in less than 10 seconds.

The volume of solvent removed and replaced was calculated by weighing the vial before and after each perturbation. Concentrations after perturbations were determined by mass balance (equations 14 and 15):

Table 2 : Summary data for the desorption rate studies

TABLE CONTAIN	# SPHERES			MASS	VOL.
	LARGE	MEDIUM	SMALL	WAX (g)	Solvent Vol. (ml)
NP - LA	21	—	—	1.98	20.02
NP - LB	21	—	—	1.98	19.97
NP - MA	—	29	—	1.98	19.94
NP - MB	—	29	—	1.97	20.01
NP - SA	—	—	68	1.98	20.08
NP - SB	—	—	69	2.00	19.94
NP - EMA	7	10	23	1.98	20.01
NP - EMB	7	10	23	2.00	20.07
NP - NEMA	3	4	51	1.99	19.86
NP - NEMB	3	4	51	1.99	20.01
RMRC - LA	21	—	—	1.98	20.08
RMRC - LB	21	—	—	1.98	20.06
RMRC - EMA	7	10	23	2.00	20.09
RMRC - EMB	7	10	23	1.99	20.08
RMRC - NEMA	3	4	51	1.99	20.00
RMRC - NEMB	3	4	51	1.98	20.02
RMRS - LA	21	—	—	1.96	19.99
RMRS - LB	21	—	—	1.97	20.07
RMRS - MA	—	29	—	1.97	20.04
RMRS - MB	—	29	—	1.96	19.99
RMRS - SA	—	—	69	2.00	20.06
RMRS - SB	—	—	69	2.01	19.97
RMRS - EMA	7	10	23	1.99	19.93
RMRS - EMB	7	10	23	1.99	20.04
RMRS - NEMA	3	4	52	2.01	20.15
RMRS - NEMB	3	4	49	1.90	20.02
RARC - LA	21	—	—	1.96	19.95
RARC - LB	20	—	—	1.93	20.12
RARC - MA	—	29	—	1.97	19.96
RARC - MB	—	28	—	1.95	20.00
RARC - SA	—	—	69	2.00	20.02
RARC - SB	—	—	69	2.00	20.03
RARC - EMA	7	10	23	1.98	20.10
RARC - EMB	7	10	23	1.99	20.15
RARC - NEMA	3	4	52	2.00	20.17
RARC - NEMB	3	4	52	2.00	20.03
RARCS - LA	20	—	—	1.94	20.10
RARCS - LB	20	—	—	1.91	19.95
RARCS - EMA	7	10	23	2.00	20.07
RARCS - EMB	7	10	23	1.99	20.07
RARCS - NEMA	3	4	52	1.99	20.09
RARCS - NEMB	3	4	52	1.99	19.96

$$V_{\text{after adding}} = V_{\text{initial}} - V_{\text{removed}} + V_{\text{adding}} \quad (14)$$

$$C_{\text{after adding}} = \frac{C_{\text{initial}}(V_{\text{initial}} - V_{\text{removed}}) + C_{\text{adding}}V_{\text{adding}}}{V_{\text{after adding}}} \quad (15)$$

Each experiment was performed in duplicate. Solutions were kept continuously mixed by use of a shaken or rotating table. All weights recorded were made using Ohaus analytical balance (reproducibility +/- 0.02 mg), and amber bottles were used to minimize photodegradation of anthracene. The temperature in the laboratory was kept at a relatively constant 25 °C.

The batch experiment desorption process was monitored by periodically removing a small sample of solvent from the vials, and analyzing with HPLC. After removing a sample, the boundary conditions are redetermined by the weighing process. The boundary conditions were further perturbed by removing and replacing solvent in some of the vials. The diffusion coefficient and geometric parameters (λ and δ_{max}) could be determined for all experiments as long as the mix of bead sizes was the same. By simultaneously fitting parameters for experiments subjected to different perturbation, we hoped to reduce the uncertainty of parameter estimates observed by deVenoge (1996).

IV. DATA DESCRIPTION AND ANALYSIS

Estimates of Initial Concentration in Wax

Paraffin spheres containing anthracene used in this study were made by alternatively heating and molding the wax. Heating the paraffin-anthracene mixture may have volatilized anthracene from the wax. Estimates of initial concentration of anthracene in the paraffin, C_{s_i} , obtained from different sources were compared versus heating time; these sources were serial dilution (mass balance calculation), fitting rate data from different sizes of uniform spheres, and the isotherm data set. The C_{s_i} estimates from rate data were obtained from the MSS model using a partitioning coefficient value of 9.24 $\mu\text{l}/\text{mg}$ (deVenoge, 1996), and fitting both C_{s_i} and diffusion coefficient. The C_{s_i} estimate from the isotherm data set was obtained by adjusting C_{s_i} to force the isotherm through a zero intercept. The C_{s_i} estimates versus heating time is provided in Table 3. The summary of fitted rate data is provided in Table 4.

Table 3: Estimates of initial concentration of anthracene in paraffin compared to heating time

Sample	Approximate Heating Time	# Spheres	Method of Estimate	C_{s_i} ($\mu\text{g}/\text{g}$)
Before making spheres	< 1 hour	-	Serial Dilution	19.74
Large Spheres	~ 8 hours	307	Rate Data Fitting	17.94 ~19.21
Medium Spheres	~ 9 hours	313	Rate Data Fitting	17.07 ~ 19.21
Small Spheres	~ 40 hours	1156	Rate Data Fitting	16.44 ~17.06
Isotherm Wax	> 40 hours	-	Isotherm data	16.08

Table 4: Initial concentration of anthracene in wax from fitting individual rate experiment data

Experiment Types	Cs _i		
	Large Spheres	Medium Spheres	Small Spheres
NP - A	18.56	Discarded	17.06
NP - B	17.95	19.21	16.85
RMRC - A	17.94	-	-
RMRC - B	18.06	-	-
RMRS - A	18.84	19.03	16.89
RMRS - B	19.1	19.10	16.78
RARC - A	18.59	19.08	16.44
RARC - B	17.99	19.10	16.49
RARCS - A	19.58	-	-
RARCS - B	19.62	-	-
MEAN	18.623	19.10	16.752

Data in table 3 suggests that longer heating time resulted in lower anthracene concentration in paraffin. Several reasons help clarify why paraffin used for different sized spheres and the isotherm experienced different heating times:

1. When paraffin was heated and melted ready to mold, the paraffin was removed from the heater. Since smaller spheres tended to be more difficult to turn and shape, it required more time to reheat and remelt the paraffin after the paraffin was cooled.
2. Three times as many small spheres were required for experiments compared to the number of large and medium spheres. Thus, wax used for small spheres needed longer time to reheat and more reheating cycles. Also, the small spheres were created from residual wax left after making large and medium spheres because we were running out of paraffin.
3. Isotherm batch paraffin was prepared after finishing small spheres; therefore, a longer heating time and lower Cs_i than any other sources would be expected.

Estimate of Isotherm

The shredded paraffin batch experiment used to estimate desorption equilibrium was analyzed after 21 days. A linear isotherm was observed (Figure 3); the partition coefficient (K_p) was estimated as $10.4 \mu\text{l}/\text{mg}$ from the slope of the isotherm.

Since paraffin was considered to have a flexible rubbery structure, a linear, reversible isotherm for sorption and desorption processes was expected. The K_p value should be the same for sorption and desorption. deVenoge (1996) conducted sorption studies using the same materials and methods as used in this research, and came up with an average $K_p = 9.24 \mu\text{l}/\text{mg}$. The sorption process reached equilibrium in approximately 18 days. The sorption and desorption K_p values are similar; however, the desorption isotherm did not have a zero intercept like sorption isotherm. Hysteresis was unlikely for this system, and would probably not have produced a linear relationship in Figure 3. Therefore, the cause of non-zero intercept was assumed to be a bad estimate of the initial concentration in paraffin, C_{s_i} . The desorption isotherm was adjusted to fit the zero intercept by changing C_{s_i} from $19.74 \mu\text{g}/\text{g}$ to $16.08 \mu\text{g}/\text{g}$.

This adjusted C_{s_i} value agrees with estimates from fitting rate data, and is logical in the context of heating procedures used in these experiments. Adjusting the C_{s_i} value also allows the preservation of the assumption that sorption and desorption are linear reversible processes in paraffin. In future experiments, the initial concentration in the wax should be verified by an independent analysis.

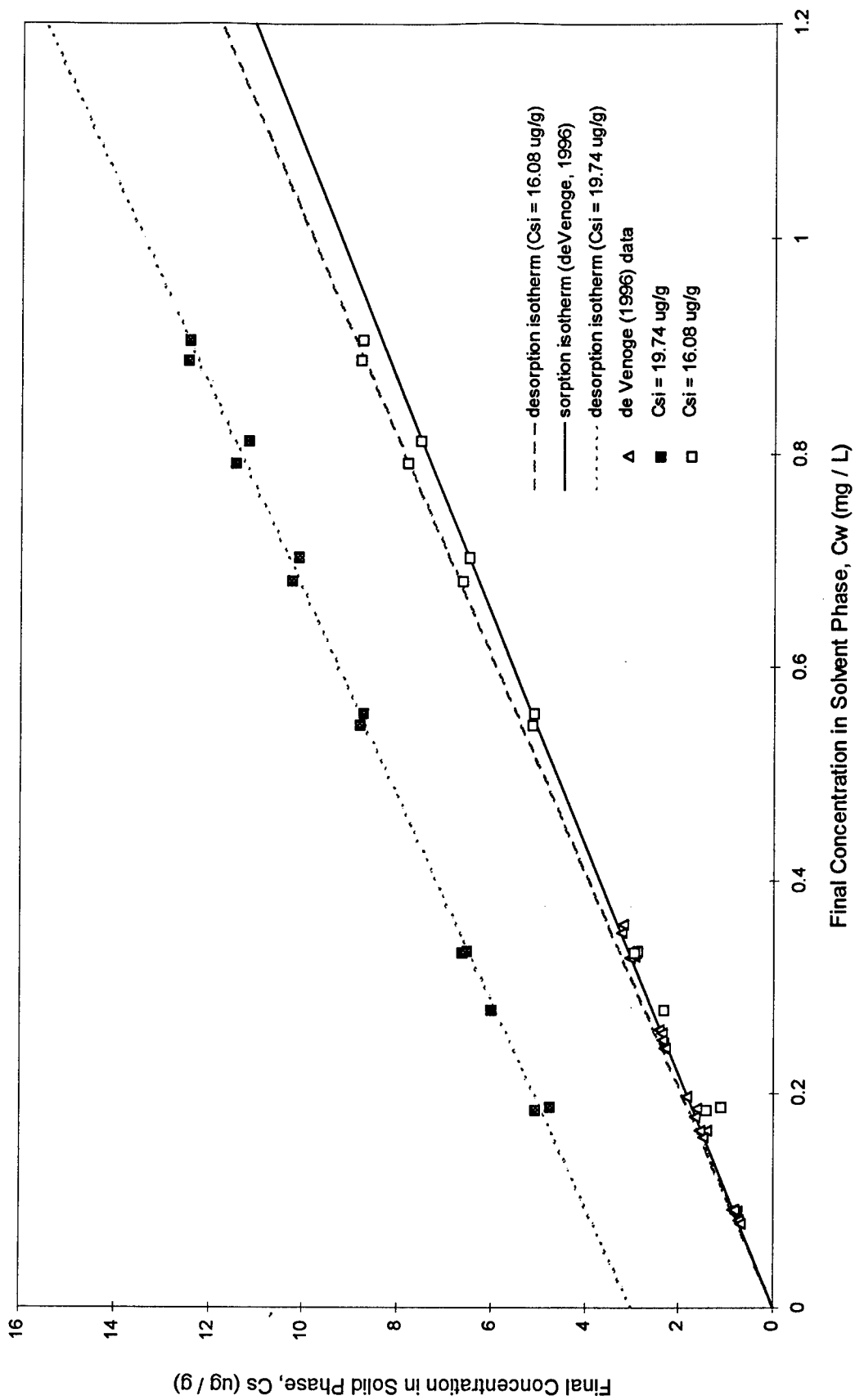


Figure 3: Desorption and sorption isotherm.

Diffusion Coefficient

The effective diffusion coefficient, D_{eff} , was estimated from rate experiments with uniform-sized spheres using the MSS model. Estimates were obtained first for individual experiments. Later, all experiments with a given sized of paraffin sphere were fitted for D_{eff} and C_{s_i} simultaneously; the averages of D_{eff} and C_{s_i} were used in predicting diffusion path length, δ_{max} , and shape factor, λ . In all parameter predictions of MSS model, the partition coefficient, K_p , was fixed at 9.24 $\mu\text{l}/\text{mg}$. This sorption K_p value was used because of uncertainty of C_{s_i} in desorption isotherm.

The D_{eff} was estimated separately for each experiment; the mean for all aliquots was first calculated as $1.573 \times 10^{-8} \text{ cm}^2/\text{sec}$. A statistical analysis of 95 % confidence intervals was conducted; evidence showed that every individual D_{eff} from aliquot hooked the mean. However, one experiment (NP-MA) had a very high sum of square for error and standard deviation, demonstrating a poor parameter estimate. This sample was excluded from later discussion. The mean of D_{eff} was recalculated as $1.501 \times 10^{-8} \text{ cm}^2/\text{sec}$. The fitted D_{eff} for individual uniform size experiments are provided in Figure 4.

The means of fitted D_{eff} values for different uniform sizes of spheres were also compared using ANOVA Single Factor analysis; the results showed a strong evidence that D_{eff} among all uniform spheres had no significant differences without including NP-MA. The fitted D_{eff} values are shown in Table 5; detailed fitted D_{eff} data is provided in Appendix C. The ANOVA analysis is provided in Table 6.

The experiments for the same sized beads were fitted simultaneously, and the resulting estimates of D_{eff} are provided in Table 7, along with the estimates of D_{eff}

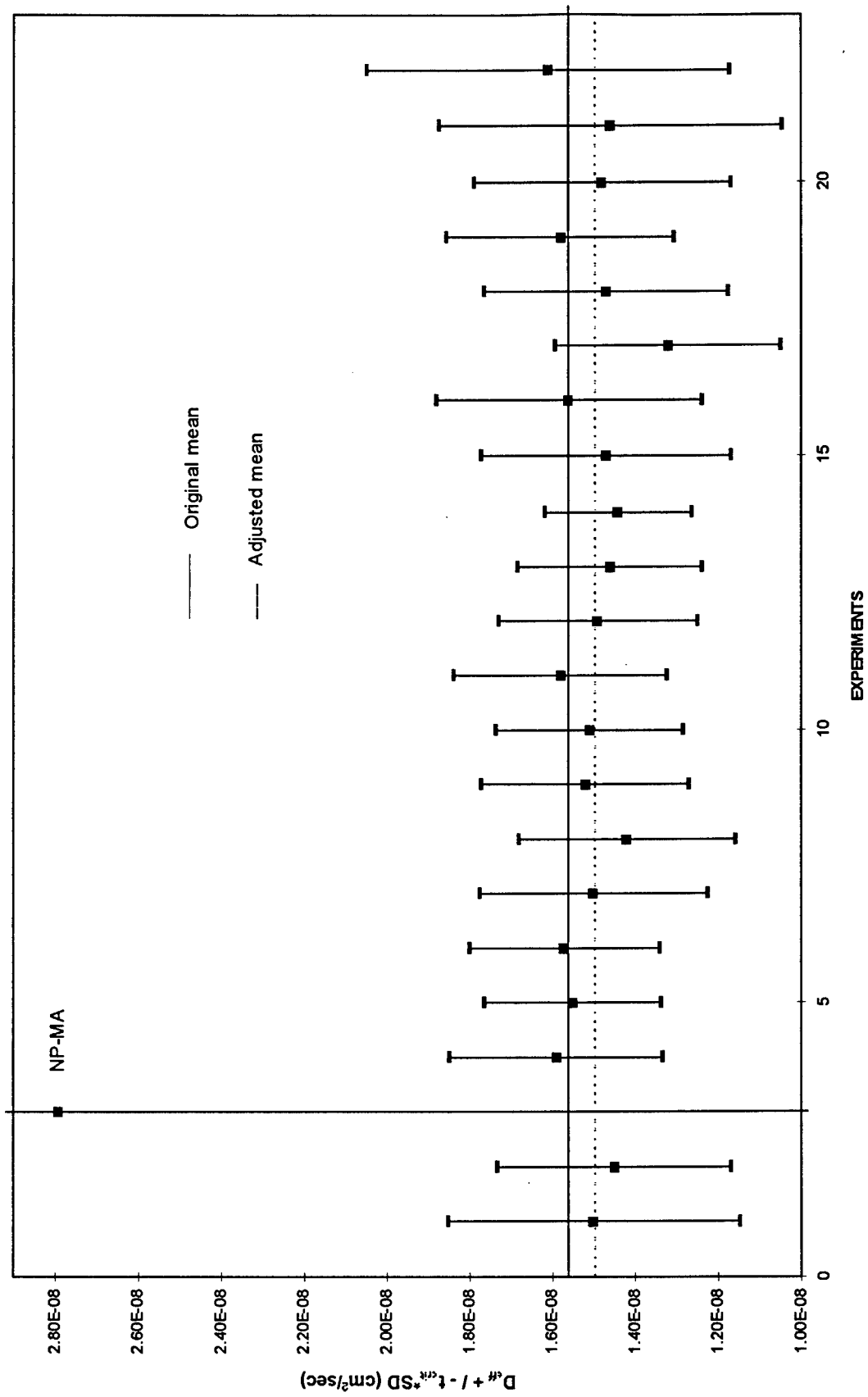


Figure 4: Fitted D_{eff} for individual uniform-sized experiments

from the data of deVenoge (1996). The comparison of D_{eff} between sorption and desorption is provided in Figure 5.

Table 5: Summary of fitted diffusion coefficient

Experiment Types	SPHERE SIZES		
	LARGE	MEDIUM	SMALL
NP - A (SD)	1.50E-08 (1.60E-09)	2.79E-08 (3.85E-08)	1.55E-08 (9.76E-10)
NP - B (SD)	1.45E-08 (1.25E-09)	1.59E-08 (1.17E-09)	1.57E-08 (1.01E-09)
RMRC - A (SD)	1.50E-08 (1.26E-09)	-	-
RMRC - B (SD)	1.42E-08 (1.20E-09)	-	-
RMRS - A (SD)	1.52E-08 (1.15E-09)	1.58E-08 (1.18E-09)	1.46E-08 (1.02E-09)
RMRS - B (SD)	1.51E-08 (1.04E-09)	1.49E-08 (1.10E-09)	1.44E-08 (8.12E-10)
RARC - A (SD)	1.47E-08 (1.48E-09)	1.32E-08 (1.33E-09)	1.58E-08 (1.35E-09)
RARC - B (SD)	1.56E-08 (1.57E-09)	1.47E-08 (1.44E-09)	1.48E-08 (1.52E-09)
RARCS - A (SD)	1.46E-08 (2.03E-09)	-	-
RARCS - B (SD)	1.61E-08 (2.15E-09)	-	-

Note: standard deviation (SD) for each experiment is included in this table.

Table 6: ANOVA analysis of effective diffusion coefficient

Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		
LARGE	10	1.50E-07	1.50E-08	3.10E-19		
MEDIUM	5	7.45E-08	1.49E-08	1.20E-18		
SMALL	6	9.08E-08	1.50E-08	3.70E-19		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1.52E-19	2	7.62E-20	0.14694	0.86437	3.55456
Within Groups	9.33E-18	18	5.19E-19			
Total	9.49E-18	20				

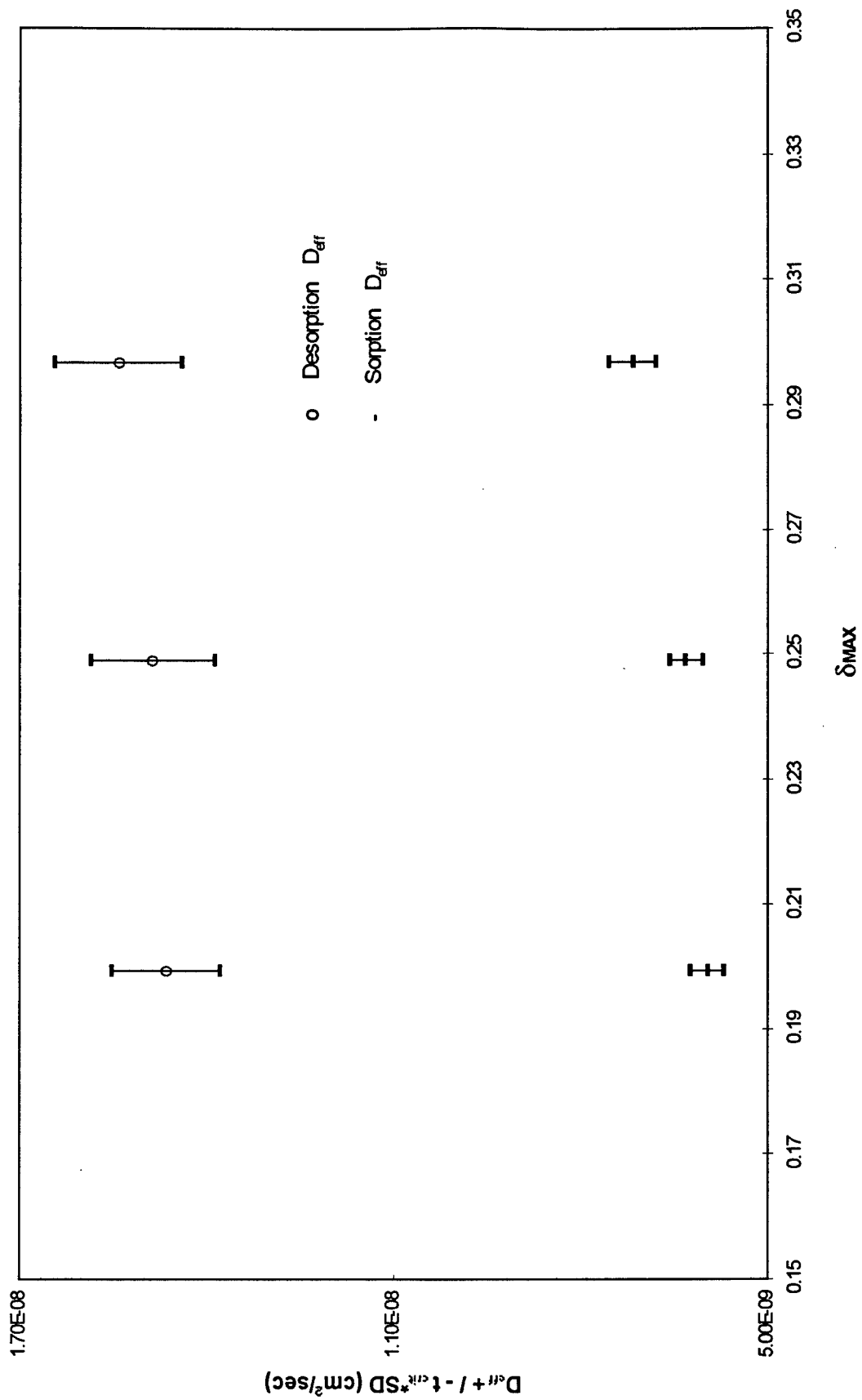


Figure 5: Effective diffusion coefficients from sorption and desorption experiments

Table 7: Estimates of effective diffusion coefficients from sorption and desorption experiments

Sphere	Effective Diffusion Coefficient (cm ² /sec)	
Radius (cm)	Sorption (deVenoge, 1996)	Desorption (this study)
0.1994 (SD)	5.96E-09 (1.30E-10)	1.47E-08 (4.36E-10)
0.2490 (SD)	6.30E-09 (1.32E-10)	1.49E-08 (5.02E-10)
0.2970 (SD)	7.16E-09 (1.88E-10)	1.54E-08 (5.16E-10)

The desorption D_{eff} estimates are slightly greater than twice the rate of the D_{eff} values estimated from sorption experiments. deVenoge's (1996) sorption experiments were conducted for 45 days, the desorption experiments in this study lasted between 69 and 85 days. A reasonable expectation might be that diffusion coefficients would be over-estimated for shorter duration experiments, but obviously the opposite effect was observed here.

deVenoge (1996) suggested that the increase in diffusion coefficient with bead size observed in his experiments could be caused by solvation of the paraffin during the course of the experiment. The higher diffusion coefficients observed in the desorption data may be caused by collection of more data at longer times (more complete paraffin solvation). The expectation would be that this effect would be more pronounced in experiments that were subjected to repeated perturbations (RARC and RARCS experiments). Table 5 however demonstrates that all experiments observed approximately the same diffusion coefficient. The cause of the larger diffusion coefficient for desorption experiments is therefore not clear.

Another possibility for the difference between sorption and desorption coefficients involves the paraffin shapes. This study and deVenoge (1996) used the same paraffin type (CAS number 8002-74-2), but from different lots (lot 03325CQ and lot 09601KN respectively). Differences in paraffin sorbent might also be caused by subtle differences in bead manufacturing processes. If deVenoge (1996) created a transfers-resistant film on his beads, or if small fractures were formed in the beads used in this study, differences in diffusion coefficients might result.

Sorption Capacity Distribution

All evenly mixed (EM) non-evenly mixed (NEM) experiments were fitted simultaneously in MSS model to fit diffusion path length, δ_{\max} , and shape factor, λ , so as to predict frequency distribution of the sorption site, using $K_p = 9.24 \mu\text{l/mg}$, $D_{\text{eff}} = 1.501\text{E-}08 \text{ cm}^2/\text{sec}$. Initial concentration, C_{s_i} , was fixed at $18.42 \mu\text{g/g}$ for EM experiments, and $17.87 \mu\text{g/g}$ for NEM experiments. C_{s_i} was calculated based on mass fraction of different sized spheres which have different concentrations estimated in the beginning of this chapter. The summary fitted results are provided in Table 8. The predicted distributions were compared to true distribution along average diffusion path length; the comparisons are provided in Figure 6 and 7.

Table 8: Summary of fitted geometry parameters

Experiments	δ_{\max} (cm)	λ
ALL-EM (SD) [SSQ for Error]	0.13392 (0.05542) [3.18]	0.41153 (0.77856) [3.18]
ALL-NEM (SD) [SSQ for Error]	0.13231 (0.01409) [0.154]	0.56774 (0.21821) [0.154]

Table 8 reveals that the MSS model failed to predict the sorption site distribution. This may be due to a poor estimate of input $C_{s,i}$. Given the uncertainty of $C_{s,i}$, variance in initial concentration on individual spheres could complicate and interfere with geometry parameter prediction. Also, the model attempts to fit two parameters simultaneously. Unfortunately, there are a continuum of possible answers. The failure of the MSS model is therefore attributed to the inability of the model to determine a unique solution from a continuum of possibility.

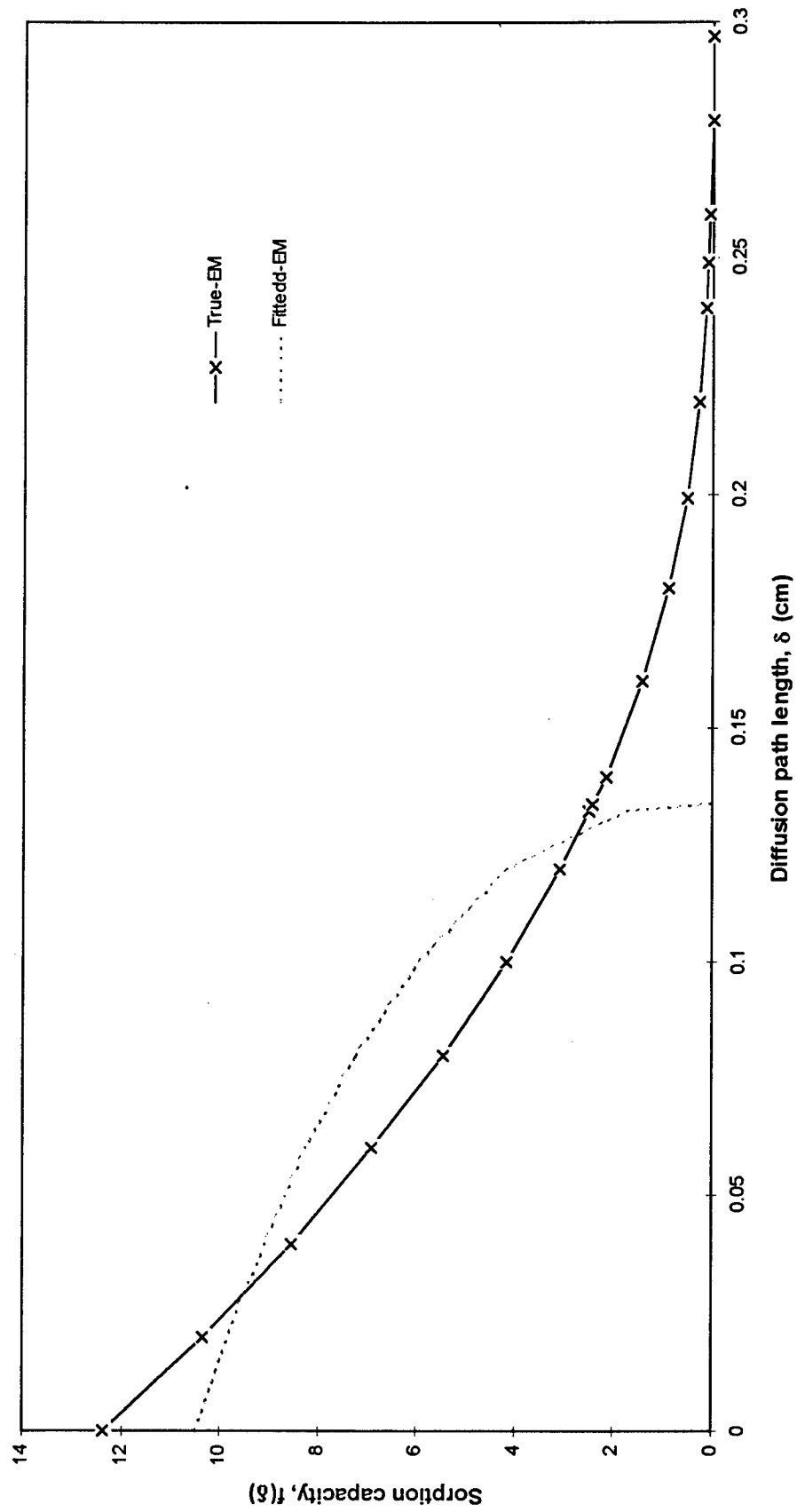


Figure 6: Fitted and true sorption capacity distribution for evenly mixed experiments

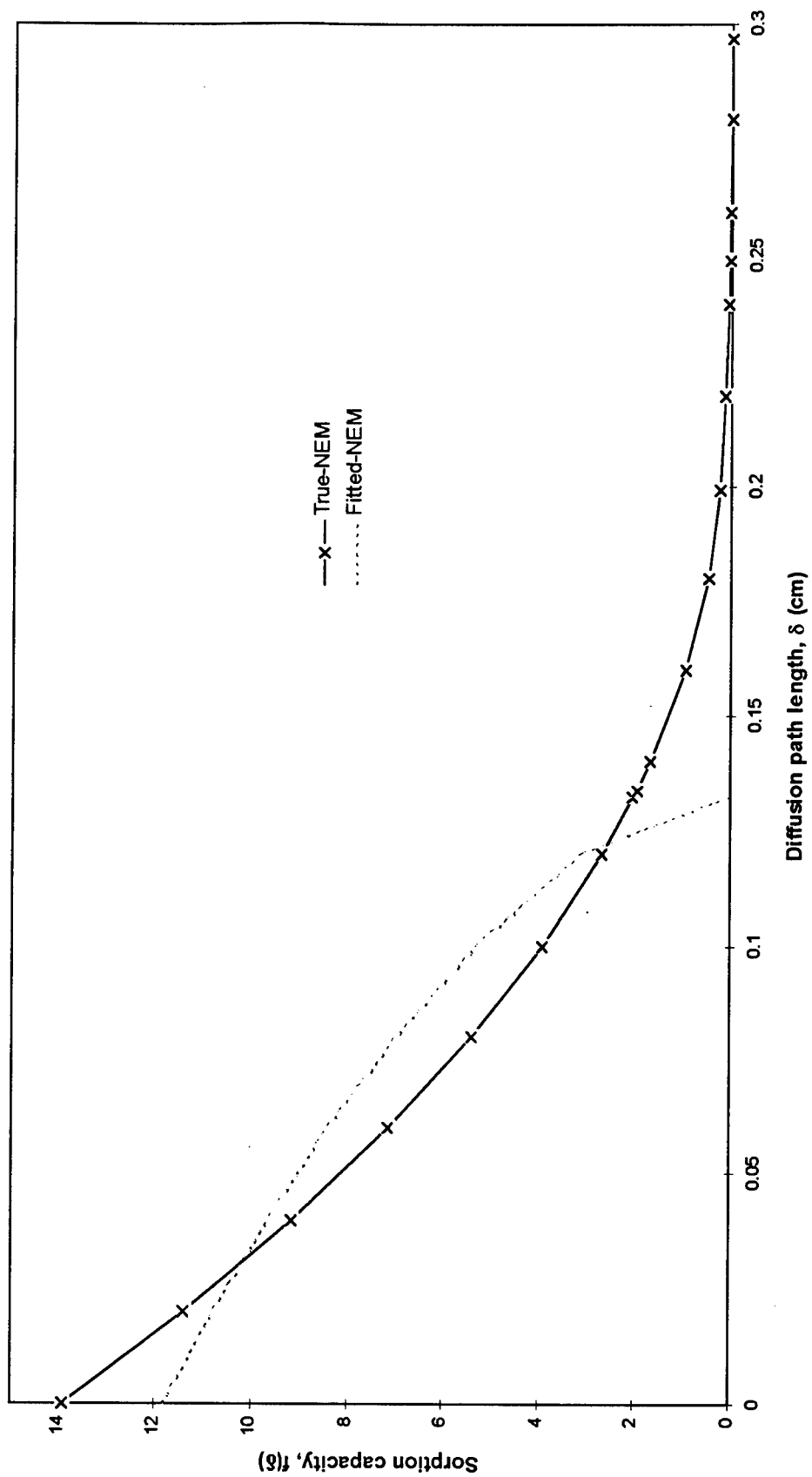


Figure 7: Fitted and true sorption capacity distribution for non-evenly mixed experiments

V. CONCLUSIONS AND RECOMMENDATIONS

Techniques were developed to study desorption behavior. Results were compared to a sorption study (deVenoge, 1996) to determine if sorption and desorption were reversible processes for anthracene partitioning between paraffin and methanol / water. Lastly, MSS model was used to predict sorption site distribution parameters from desorption rate data.

Paraffin spheres needed in this study were made by alternatively heating and molding. Apparent loss of anthracene from the wax is attributed to volatilization due to heating. Longer heating time also suggested more loss of anthracene from paraffin.

A linear isotherm and yielding similar partition coefficient, K_p , to the sorption study by deVenoge (1996) were obtained; however the isotherm had a non-zero intercept. If heating the paraffin does affect the initial concentration of anthracene in paraffin, adjustments can be made and there is evidence that sorption and desorption are reversible processes for this system. Consistent fitted diffusion coefficient values were obtained for different uniform-sized paraffin spheres, indicating that the diffusion coefficient was independent of sphere size. However, the diffusion coefficient for desorption was also found to be faster than that for sorption (deVenoge, 1996). A reason for the faster diffusion coefficient could not be determined.

The MSS model was not able to successfully fit sorbent geometry. This is likely caused by a lack of uniqueness in model parameters, and is likely to have been complicated further by a poor estimate of initial concentration.

Future desorption studies should focus on developing better techniques to overcome potential losses of anthracene by heating the paraffin. Better estimates of initial concentration would increase confidence in assumptions and fitted parameters. Indirect heating paraffin processes such as putting the container of paraffin in bigger container with heated water might be a way to solve this problem. Heating time posed a potential problem estimating C_{s_i} in this study; thus, heating time should be limited as much as possible. Also, residual wax after molding should not be reused.

Analysis of controls indicated instrumental fluctuations during this study. A better way to account for instrumental fluctuations could be calibrating the HPLC for every round of analyses. Further, a large syringe (20-50 ml volume) could be used to remove solvent during perturbations, which would preclude paraffin from contacting filter paper. This might reduce error.

The D_{eff} for this study was found to be faster than that for the sorption study. For further sorption and desorption studies, it is recommended that the effects of solvation of paraffin and solvation time on the D_{eff} be examined.

GLOSSARY

C_w	Concentration of anthracene in the solvent, $M L^{-3}$
C_s	Concentration of anthracene in the solid phase, $M M^{-1}$
D_{eff}	Effective diffusion coefficient, $L^2 t^{-1}$
F	The fraction of fast or equilibrium sites
$f(\delta)$	Frequency distribution of sorption capacity in the sorbed sites
i	Initial
j	Compartment designator
k_2	The mass transfer rate constant, $L^3 M^{-1}$
K_p	Equilibrium partition coefficient, $L^3 M^{-1}$
r	Radius of the sorbent, L
S_1	The sorbed concentrations in fast sites, $M M^{-1}$
S_2	The sorbed concentrations in slow sites, $M M^{-1}$
t	Time, t
δ	Diffusion path length, L
λ	Shape factor

Appendix A

HPLC Calibration Curve

Five known amounts of anthracene were used as standards to describe the calibration curve to convert peak area to anthracene mass or concentration. The five level standard calibration is shown in Table A-1.

Table A-1 : Five level calibration

5 point Calibration	1	2	3	4	5
Average Mass of 2 Estimates	1.148	2.870	5.740	11.48	17.22
Peak Area	14.3839	40.6224	81.4019	158.773	236.63

This five level calibration gave a linear relationship with a correlation 0.9999 between peak area 14 to 236; the calibration curve is provided in figure A-1.

The calibration curve for the concentration of anthracene in aliquot solution is therefore described by its slope:

$$y = \frac{mx}{\phi} + b$$

where ϕ is the injected volume of the sample ranging from 0.1 to 25 μl .

y = peak area

m = slope

x = mass of anthracene

b = intercept of the slope

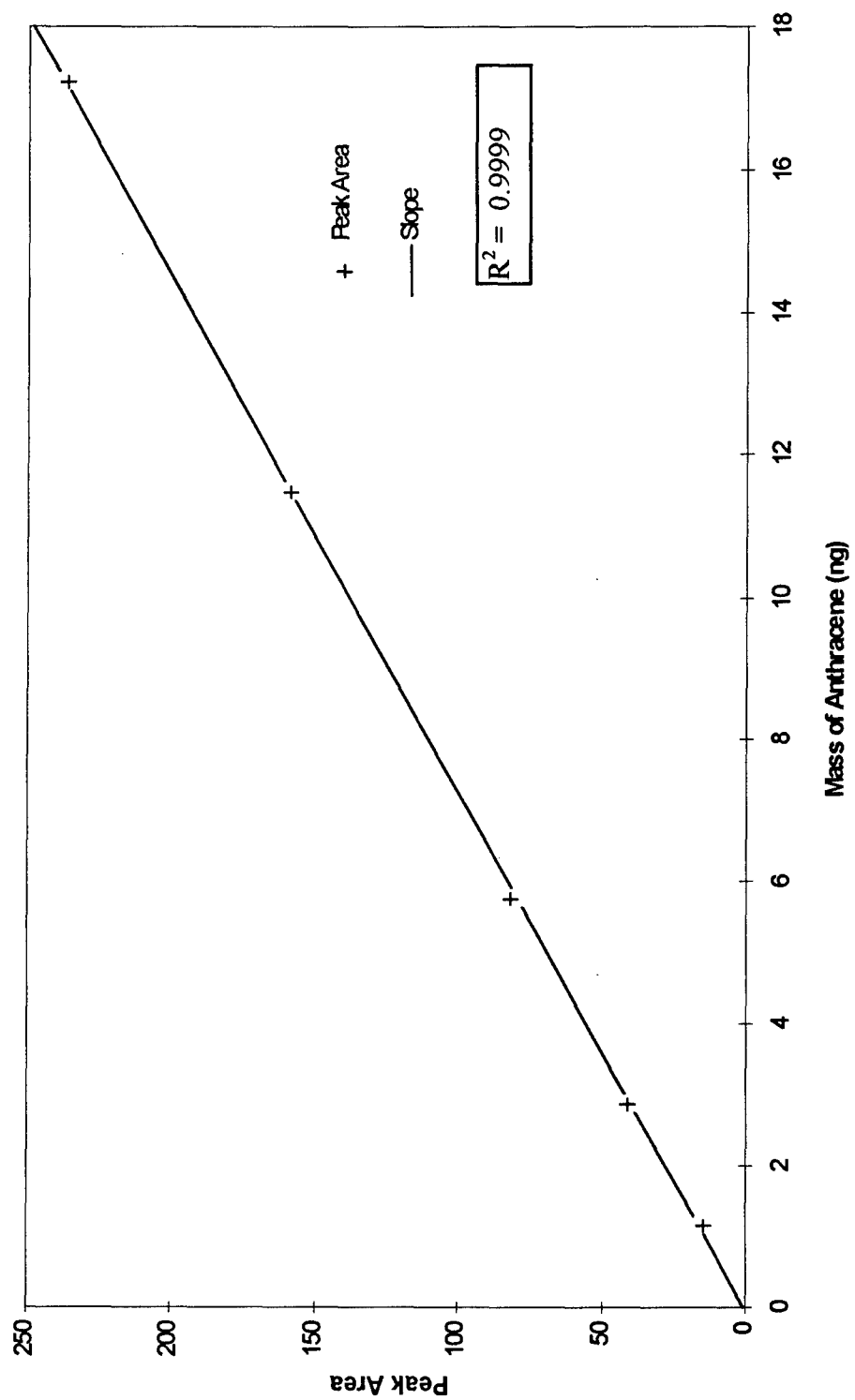


Figure A -1 : Five Level Calibration Curve

APPENDIX B

Analysis of Controls

Three controls were conducted and compared using the same chart (figure B-1). The variation in concentration was studied versus time. In most of the control, the variation was not large. However, in Control 1, a fluctuation was consistently observed either up or down compared to the rest of controls. This phenomenon probably can be attributed to instrument's fluctuation.

A hypothesis of that sequentially opening vials cause evaporation of methanol was reviewed. A replicate of control 3 was prepared, sealed, and analyzed at the last sampling day along with control 3 to compare the difference between opening vials and not opening the vials until the end of the experiment. Consistent results suggest that opening vials had no significant effect in this experiment.

Since an instrument fluctuation was observed, controls needed to be normalized and rate data adjusted. The average of two point estimates used as true mean was taken from each control 2 and 3 right after the HPLC was recalibrated. Several means were determined from different populations of control 2 and 3 according to sample's consistency. Factors were found in each population by comparing the ratio of the true mean and the mean of each population. Lastly, the factor generated in each population was used to multiply all observations in that population. Normalized control 2 and 3 are provided in Figure B-2.

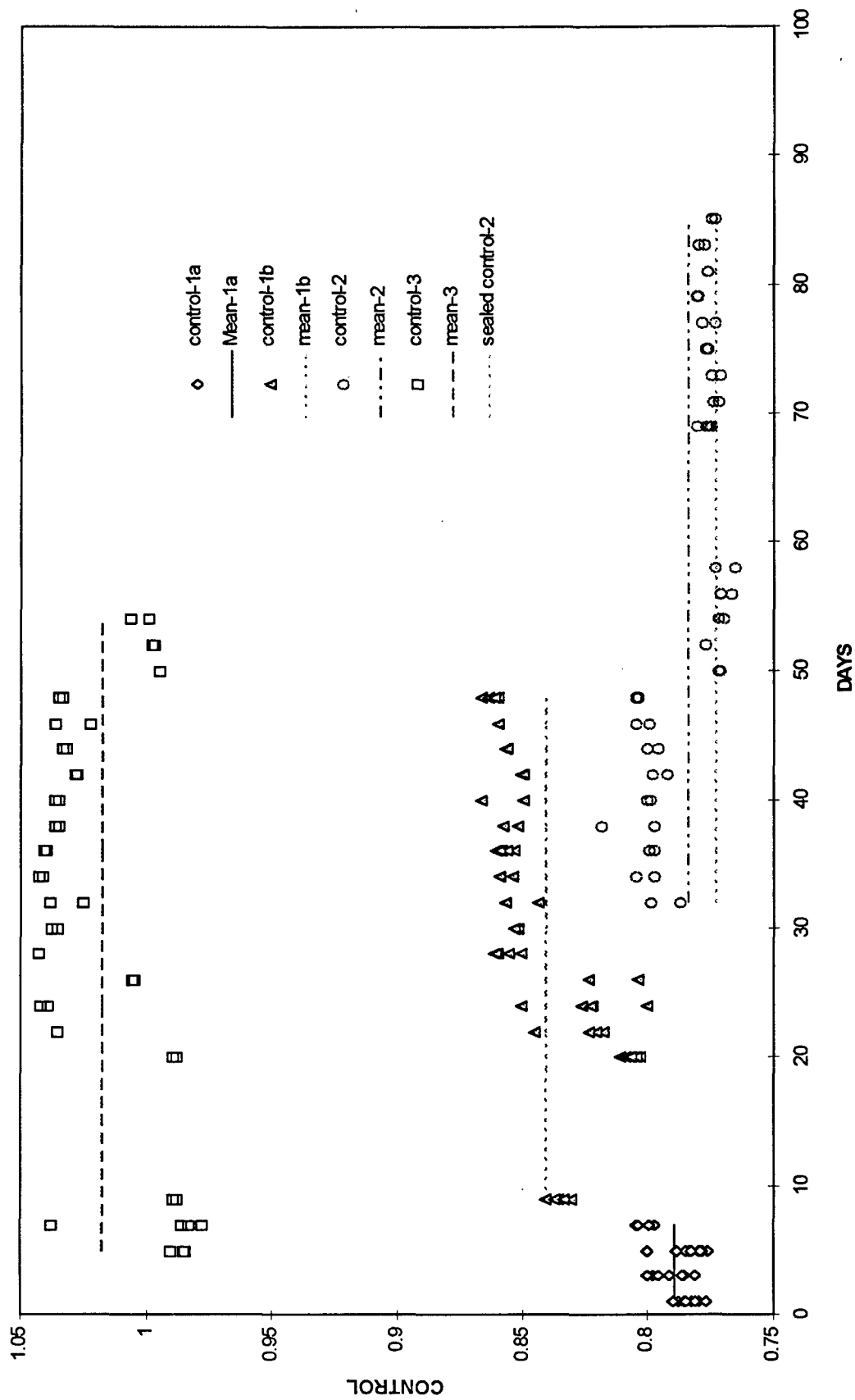


Figure B-1: Control analysis before normalization

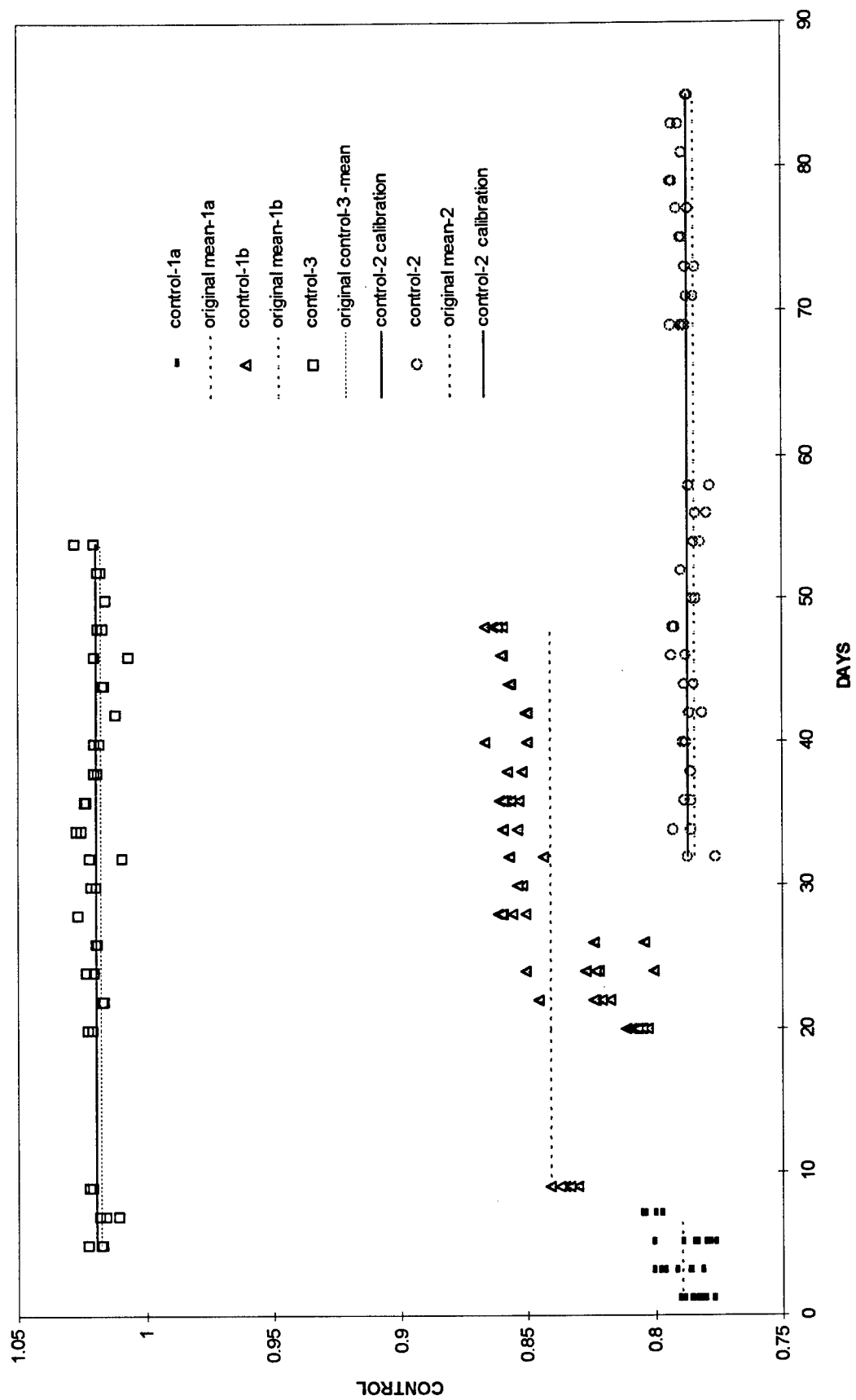


Figure B-2: Control analysis after normalization

APPENDIX C **Data Files used in MSS Model**

Hwang:	Large balls				
RKD	DEFF	DPATH	RLAM	XSS0	FAST
9.24	1.13E-08	0.297	2	19.74	0

"1 means fit parameter, 0 means keep it fixed"

0	1	0	0	1	0
---	---	---	---	---	---

"CONSTANTS(Ms,VLi,Cli,NBCC)"

10

1.975	20.016	0	11
1.975	20.016	0	11
1.9775	20.078	0	12
1.9753	20.059	0	12
1.9628	19.99	0	12
1.9708	20.071	0	12
1.9588	19.953	0	31
1.9588	19.953	0	31
1.9707	19.96	0	35
1.9439	20.097	0	35

1	59400.	0.73	0.	0.
1	232800.	0.846	0.	0.
1	465600.	0.583	0.	0.
1	640800.	0.693	0.	0.
1	809400.	0.762	0.	0.
1	1760400.	0.56	0.	0.
1	1950000.	0.906	0.	0.
1	2095200.	0.71	0.	0.
1	2438400.	0.627	0.	0.
1	3128400.	0.861	0.	0.
1	4182000.	0.634	0.	0.
2	59400.	0.73	0.	0.
2	232800.	0.846	0.	0.
2	465600.	0.583	0.	0.
2	640800.	0.693	0.	0.
2	809400.	0.762	0.	0.
2	1760400.	0.56	0.	0.
2	1950000.	0.906	0.	0.
2	2095200.	0.71	0.	0.
2	2438400.	0.627	0.	0.
2	3128400.	0.861	0.	0.
2	4182000.	0.634	0.	0.
3	59400.	0.589	0.	0.
3	232800.	0.689	0.	0.

3	465600.	0.658	0.	0.
3	640800.	15.193	16.92	0.
3	640801.	0.725	0.	0.
3	809400.	0.58	0.	0.
3	1760400.	0.45	0.	0.
3	1950000.	1.016	0.	0.
3	2095200.	0.57	0.	0.
3	2438400.	0.654	0.	0.
3	3128400.	0.756	0.	0.
3	4182000.	0.785	0.	0.
4	59400.	0.564	0.	0.
4	232800.	0.617	0.	0.
4	465600.	0.674	0.	0.
4	640800.	15.381	16.801	0.
4	640801.	0.577	0.	0.
4	809400.	0.51	0.	0.
4	1760400.	0.472	0.	0.
4	1950000.	0.91	0.	0.
4	2095200.	0.629	0.	0.
4	2438400.	0.538	0.	0.
4	3128400.	0.801	0.	0.
4	4182000.	0.705	0.	0.
5	59400.	0.455	0.	0.
5	232800.	0.562	0.	0.
5	465600.	0.582	0.	0.
5	640800.	15.43	17.299	1.019
5	640801.	0.693	0.	0.
5	809400.	0.461	0.	0.
5	1760400.	0.461	0.	0.
5	1950000.	0.643	0.	0.
5	2095200.	0.49	0.	0.
5	2438400.	0.625	0.	0.
5	3128400.	0.836	0.	0.
5	4182000.	0.732	0.	0.
6	59400.	0.703	0.	0.
6	232800.	0.59	0.	0.
6	465600.	0.601	0.	0.
6	640800.	15.685	17.377	1.019
6	640801.	0.352	0.	0.
6	809400.	0.467	0.	0.
6	1760400.	0.465	0.	0.
6	1950000.	0.766	0.	0.
6	2095200.	0.492	0.	0.
6	2438400.	0.59	0.	0.
6	3128400.	0.678	0.	0.

6	4182000.	0.735	0.	0.
7	59400.	0.656	0.	0.
7	232800.	0.645	0.	0.
7	465600.	0.592	0.	0.
7	640800.	17.208	19.106	0.
7	640801.	0.423	0.	0.
7	809400.	0.457	0.	0.
7	1760400.	18.486	19.433	0.
7	1760401.	0.709	0.	0.
7	1950000.	0.798	0.	0.
7	2095200.	0.463	0.	0.
7	2265000.	0.762	0.	0.
7	2438400.	17.189	19.872	0.
7	2610000.	0.883	0.	0.
7	2784000.	0.842	0.	0.
7	2931000.	0.839	0.	0.
7	3128400.	16.869	20.021	0.
7	3301200.	0.802	0.	0.
7	3474900.	0.715	0.	0.
7	3646800.	0.872	0.	0.
7	3822900.	11.679	13.047	0.
7	3992400.	0.819	0.	0.
7	4182000.	0.625	0.	0.
7	4342200.	0.712	0.	0.
7	4513500.	0.787	0.	0.
7	4686600.	0.746	0.	0.
7	4856400.	0.759	0.	0.
7	5043300.	0.669	0.	0.
7	5981400.	14.177	20.134	0.
7	6330000.	0.78	0.	0.
7	6676200.	0.823	0.	0.
7	7020000.	0.826	0.	0.
8	59400.	0.56	0.	0.
8	232800.	0.642	0.	0.
8	465600.	0.541	0.	0.
8	640800.	17.64	19.265	0.
8	640801.	0.445	0.	0.
8	809400.	0.467	0.	0.
8	1760400.	18.38	19.209	0.
8	1760401.	0.709	0.	0.
8	1950000.	0.798	0.	0.
8	2095200.	0.463	0.	0.
8	2265000.	0.872	0.	0.
8	2438400.	17.189	19.924	0.
8	2610000.	0.841	0.	0.

8	2784000.	0.803	0.	0.
8	2931000.	0.834	0.	0.
8	3128400.	17.247	20.026	0.
8	3301200.	0.891	0.	0.
8	3474900.	0.795	0.	0.
8	3646800.	0.78	0.	0.
8	3822900.	9.298	14.973	0.
8	3992400.	0.729	0.	0.
8	4182000.	0.631	0.	0.
8	4342200.	0.656	0.	0.
8	4513500.	0.691	0.	0.
8	4686600.	0.726	0.	0.
8	4856400.	0.641	0.	0.
8	5043300.	0.651	0.	0.
8	5981400.	18.513	20.048	0.
8	6330000.	0.727	0.	0.
8	6676200.	0.748	0.	0.
8	7020000.	0.859	0.	0.
9	59400.	0.564	0.	0.
9	232800.	0.552	0.	0.
9	465600.	0.578	0.	0.
9	640800.	18.568	19.517	1.019
9	640801.	0.586	0.	0.
9	809400.	0.494	0.	0.
9	1760400.	18.456	19.405	1.019
9	1760401.	0.625	0.	0.
9	1950000.	0.778	0.	0.
9	2095200.	0.545	0.	0.
9	2265000.	0.68	0.	0.
9	2438400.	17.239	19.887	1.019
9	2610000.	0.784	0.	0.
9	2784000.	0.823	0.	0.
9	2931000.	0.857	0.	0.
9	3128400.	17.221	20.137	0.
9	3301200.	0.842	0.	0.
9	3474900.	0.803	0.	0.
9	3646800.	0.628	0.	0.
9	3822900.	17.8	19.937	1.019
9	3992400.	0.712	0.	0.
9	4182000.	0.641	0.	0.
9	4342200.	0.709	0.	0.
9	4513500.	17.894	20.108	0.
9	4686600.	0.741	0.	0.
9	4856400.	0.744	0.	0.
9	5043300.	0.579	0.	0.

9	5981400.	18.032	20.01	1.019
9	6154200.	0.726	0.	0.
9	6330000.	1.068	0.	0.
9	6499800.	0.784	0.	0.
9	6676200.	17.465	20.086	0.
9	6849000.	0.786	0.	0.
9	7020000.	0.797	0.	0.
9	7189200.	0.874	0.	0.
10	59400.	0.604	0.	0.
10	232800.	0.632	0.	0.
10	465600.	0.621	0.	0.
10	640800.	18.632	19.418	1.019
10	640801.	0.553	0.	0.
10	809400.	0.536	0.	0.
10	1760400.	18.632	19.418	1.019
10	1760401.	0.472	0.	0.
10	1950000.	0.776	0.	0.
10	2095200.	0.474	0.	0.
10	2265000.	0.67	0.	0.
10	2438400.	17.628	20.09	1.019
10	2610000.	0.678	0.	0.
10	2784000.	0.75	0.	0.
10	2931000.	0.816	0.	0.
10	3128400.	17.637	20.104	0.
10	3301200.	0.744	0.	0.
10	3474900.	0.796	0.	0.
10	3646800.	0.699	0.	0.
10	3822900.	17.845	19.996	1.019
10	3992400.	0.731	0.	0.
10	4182000.	0.746	0.	0.
10	4342200.	0.748	0.	0.
10	4513500.	17.746	19.97	0.
10	4686600.	0.559	0.	0.
10	4856400.	0.665	0.	0.
10	5043300.	0.617	0.	0.
10	5981400.	18.178	20.151	1.019
10	6154200.	0.677	0.	0.
10	6330000.	0.773	0.	0.
10	6499800.	0.706	0.	0.
10	6676200.	18.022	19.987	0.
10	6849000.	0.751	0.	0.
10	7020000.	0.745	0.	0.
10	7189200.	0.875	0.	0.

1	0.001	
EXP	TIME(SECS)	CONCENTRATION(CL)
1	59400.	0.402
1	232800.	0.719
1	465600.	0.821
1	640800.	0.921
1	809400.	0.947
1	1760400.	0.979
1	1950000.	0.954
1	2095200.	0.931
1	2438400.	0.994
1	3128400.	0.987
1	4182000.	0.977
1	5981400.	0.948
2	59400.	0.402
2	232800.	0.719
2	465600.	0.821
2	640800.	0.921
2	809400.	0.947
2	1760400.	0.979
2	1950000.	0.954
2	2095200.	0.931
2	2438400.	0.994
2	3128400.	0.987
2	4182000.	0.977
2	5981400.	0.948
3	59400.	0.409
3	232800.	0.71
3	465600.	0.811
3	640799.	0.884
3	640802.	0.131
3	809400.	0.331
3	1760400.	0.557
3	1950000.	0.545
3	2095200.	0.55
3	2438400.	0.578
3	3128400.	0.575
3	4182000.	0.566
3	5981400.	0.551
4	59400.	0.397
4	232800.	0.704
4	465600.	0.805
4	640799.	0.882
4	640802.	0.127
4	809400.	0.323

4	1760400.	0.557
4	1950000.	0.567
4	2095200.	0.551
4	2438400.	0.577
4	3128400.	0.572
4	4182000.	0.576
4	5981400.	0.556
5	59400.	0.421
5	232800.	0.738
5	465600.	0.828
5	640799.	0.91
5	640802.	1.003
5	809400.	1.016
5	1760400.	1.048
5	1950000.	0.988
5	2095200.	1.02
5	2438400.	1.056
5	3128400.	1.051
5	4182000.	1.044
5	5981400.	1.014
6	59400.	0.415
6	232800.	0.747
6	465600.	0.851
6	640799.	0.927
6	640801.	1.008
6	809400.	1.02
6	1760400.	1.054
6	1950000.	1.021
6	2095200.	1.026
6	2438400.	1.067
6	3128400.	1.061
6	4182000.	1.044
6	5981400.	1.025
7	59400.	0.415
7	232800.	0.723
7	465600.	0.836
7	640799.	0.919
7	640802.	0.039
7	809400.	0.244
7	1760399.	0.522
7	1760402.	0.015
7	1950000.	0.17
7	2095200.	0.224
7	2265000.	0.23
7	2438399.	0.259

7	2610000.	0.084
7	2784000.	0.107
7	2931000.	0.118
7	3128399.	0.124
7	3301200.	0.041
7	3474900.	0.052
7	3646800.	0.055
7	3822899.	0.058
7	3992400.	0.031
7	4182000.	0.037
7	4342200.	0.039
7	4513500.	0.038
7	4686600.	0.04
7	4856400.	0.037
7	5043300.	0.038
7	5981399.	0.039
7	6330000.	0.014
7	6676200.	0.016
7	7020000.	0.018
7	7363800.	0.015
8	59400.	0.416
8	232800.	0.707
8	465600.	0.819
8	640799.	0.892
8	640802.	0.033
8	809400.	0.236
8	1760399.	0.497
8	1760402.	0.018
8	1950000.	0.162
8	2095200.	0.217
8	2265000.	0.219
8	2438399.	0.242
8	2610000.	0.079
8	2784000.	0.099
8	2931000.	0.109
8	3128399.	0.114
8	3301200.	0.039
8	3474900.	0.047
8	3646800.	0.054
8	3822899.	0.055
8	3992400.	0.029
8	4182000.	0.032
8	4342200.	0.033
8	4513500.	0.033
8	4686600.	0.034

8	4856400.	0.034
8	5043300.	0.034
8	5981399.	0.035
8	6330000.	0.01
8	6676200.	0.014
8	7020000.	0.015
8	7363800.	0.014
9	59400.	0.412
9	232800.	0.711
9	465600.	0.811
9	640799.	1.044
9	640802.	1.018
9	809400.	1.021
9	1760399.	1.044
9	1760402.	1.02
9	1950000.	1.041
9	2095200.	1.044
9	2265000.	1.033
9	2438399.	1.053
9	2610000.	1.036
9	2784000.	1.039
9	2931000.	1.038
9	3128399.	1.03
9	3301200.	0.352
9	3474900.	0.424
9	3646800.	0.459
9	3822899.	0.473
9	3992400.	0.838
9	4182000.	0.805
9	4342200.	0.785
9	4513499.	0.777
9	4686600.	0.025
9	4856400.	0.303
9	5043300.	0.335
9	5981399.	0.355
9	6154200.	0.823
9	6330000.	0.767
9	6499800.	0.74
9	6676199.	0.727
9	6849000.	0.22
9	7020000.	0.277
9	7189200.	0.299
9	7363800.	0.307
10	59400.	0.423
10	232800.	0.725

10	465600.	0.827
10	640799.	1.035
10	640802.	1.018
10	809400.	1.018
10	1760399.	1.035
10	1760402.	1.02
10	1950000.	1.041
10	2095200.	1.046
10	2265000.	1.031
10	2438399.	1.045
10	2610000.	1.032
10	2784000.	1.038
10	2931000.	1.036
10	3128399.	1.03
10	3301200.	0.353
10	3474900.	0.421
10	3646800.	0.453
10	3822899.	0.47
10	3992400.	0.845
10	4182000.	0.806
10	4342200.	0.789
10	4513499.	0.779
10	4686600.	0.025
10	4856400.	0.302
10	5043300.	0.33
10	5981399.	0.355
10	6154200.	0.829
10	6330000.	0.766
10	6499800.	0.74
10	6676199.	0.733
10	6849000.	0.221
10	7020000.	0.277
10	7189200.	0.302
10	7363800.	0.31

HWANG	TEST FOR	MSSFIT:vials Medium			
RKD	DEFF	DPATH	RLAM	XSS0	FAST

9.24	1.50E-08	0.249	2	19.74	0
------	----------	-------	---	-------	---

"1 means fit parameter, 0 means keep it fixed"

0	1	0	0	1	0
---	---	---	---	---	---

"CONSTANTS(Ms,VLi," CLi)

5

1.9728	20.00824	0	11
1.9696	20.0397	0	12
1.9636	19.98894	0	12
1.9707	19.95987	0	31
1.9462	19.99664	0	31

1	59400.	0.566269	0.	0.
1	232800.	0.595228	0.	0.
1	465600.	0.550217	0.	0.
1	640800.	0.613232	0.	0.
1	809400.	0.683297	0.	0.
1	1760400.	0.50141	0.	0.
1	1950000.	0.864751	0.	0.
1	2095200.	0.618438	0.	0.
1	2438400.	0.676464	0.	0.
1	3128400.	1.019523	0.	0.
1	4182000.	0.295434	0.	0.
2	59400.	0.451518	0.	0.
2	232800.	0.550217	0.	0.
2	465600.	0.58449	0.	0.
2	640800.	13.28691	15.18702	1.019145
2	640802.	0.513232	0.	0.
2	809400.	0.517354	0.	0.
2	1760400.	0.506833	0.	0.
2	1950000.	0.825488	0.	0.
2	2095200.	0.559002	0.	0.
2	2438400.	0.554989	0.	0.
2	3128400.	0.732581	0.	0.
2	4182000.	0.685629	0.	0.
3	59400.	0.598373	0.	0.
3	232800.	0.507484	0.	0.
3	465600.	0.563232	0.	0.
3	640800.	18.86557	20.35158	1.019145
3	640802.	0.483406	0.	0.
3	809400.	0.434165	0.	0.
3	1760400.	0.425488	0.	0.

3	1950000.	0.733948	0.	0.
3	2095200.	0.494035	0.	0.
3	2438400.	0.68449	0.	0.
3	3128400.	0.781453	0.	0.
3	4182000.	0.682636	0.	0.
4	59400.	0.631887	0.	0.
4	232800.	0.610412	0.	0.
4	465600.	0.613449	0.	0.
4	640800.	17.33869	19.41266	0.
4	640802.	0.492625	0.	0.
4	809400.	0.406291	0.	0.
4	1760400.	18.62584	19.32345	0.
4	1760402.	0.6218	0.	0.
4	1950000.	0.923102	0.	0.
4	2095200.	0.462473	0.	0.
4	2265000.	0.79859	0.	0.
4	2438400.	17.0744	19.90879	0.
4	2610000.	0.843275	0.	0.
4	2784000.	0.977874	0.	0.
4	2931000.	0.84013	0.	0.
4	3128400.	17.07397	19.91958	0.
4	3301200.	0.793926	0.	0.
4	3474900.	0.808254	0.	0.
4	3646800.	0.828601	0.	0.
4	3822900.	11.33209	13.00775	0.
4	3992400.	0.703189	0.	0.
4	4182000.	0.585531	0.	0.
4	4342200.	0.765878	0.	0.
4	4513500.	0.692343	0.	0.
4	4686600.	0.606887	0.	0.
4	4856400.	0.699805	0.	0.
4	5043300.	0.638232	0.	0.
4	5981400.	14.48862	20.15522	0.
4	6330000.	0.735976	0.	0.
4	6676200.	0.748492	0.	0.
4	7020000.	0.764859	0.	0.
5	59400.	0.639588	0.	0.
5	232800.	0.572126	0.	0.
5	465600.	0.661714	0.	0.
5	640800.	17.35104	19.21883	0.
5	640802.	0.44718	0.	0.
5	809400.	0.56887	0.	0.
5	1760400.	18.37754	19.37277	0.
5	1760402.	0.593601	0.	0.
5	1950000.	1.003362	0.	0.

5	2095200.	0.540672	0.	0.
5	2265000.	0.788069	0.	0.
5	2438400.	16.97256	20.09946	0.
5	2610000.	0.828633	0.	0.
5	2784000.	0.708677	0.	0.
5	2931000.	0.809761	0.	0.
5	3128400.	17.627	20.00348	0.
5	3301200.	0.824197	0.	0.
5	3474900.	0.798829	0.	0.
5	3646800.	0.816377	0.	0.
5	3822900.	9.957386	12.99549	0.
5	3992400.	0.752777	0.	0.
5	4182000.	0.615618	0.	0.
5	4342200.	0.719957	0.	0.
5	4513500.	0.665586	0.	0.
5	4686600.	0.604685	0.	0.
5	4856400.	0.70038	0.	0.
5	5043300.	0.519599	0.	0.
5	5981400.	15.92156	19.97751	0.
5	6330000.	0.70295	0.	0.
5	6676200.	0.728178	0.	0.
5	7020000.	0.760531	0.	0.

1 0.001
EXP TIME(SECS) CONCENTRATION(CL)

1	59400.	0.514834
1	232800.	0.831166
1	465600.	0.905095
1	640800.	0.970648
1	809400.	0.991049
1	1760400.	1.006721
1	1950000.	0.980123
1	2095200.	0.980426
1	2438400.	1.019736
1	3128400.	1.015001
1	4182000.	0.997517
1	5981400.	0.970468
2	59400.	0.500345
2	232800.	0.816043
2	465600.	0.900269
2	640799.	0.956799
2	640802.	1.003319
2	809400.	1.026867

2	1760400.	1.026899
2	1950000.	0.995637
2	2095200.	0.994244
2	2438400.	1.034415
2	3128400.	1.031502
2	4182000.	1.016001
2	5981400.	0.986914
3	59400.	0.473922
3	232800.	0.816514
3	465600.	0.896359
3	640799.	0.9665
3	640802.	1.020596
3	809400.	1.019307
3	1760400.	1.042197
3	1950000.	1.010346
3	2095200.	1.012566
3	2438400.	1.048947
3	3128400.	1.04535
3	4182000.	1.031472
3	5981400.	1.013519
4	59400.	0.484664
4	232800.	0.79854
4	465600.	0.90078
4	640799.	0.960386
4	640802.	0.036431
4	809400.	0.275489
4	1760399.	0.528884
4	1760402.	0.017297
4	1950000.	0.182222
4	2095200.	0.23687
4	2265000.	0.236169
4	2438399.	0.255753
4	2610000.	0.088027
4	2784000.	0.108543
4	2931000.	0.114543
4	3128399.	0.116569
4	3301200.	0.041314
4	3474900.	0.049585
4	3646800.	0.052635
4	3822899.	0.054625
4	3992400.	0.03025
4	4182000.	0.03348
4	4342200.	0.039121
4	4513500.	0.034592
4	4686600.	0.035771

4	4856400.	0.035898
4	5043300.	0.033989
4	5981399.	0.034
4	6330000.	0.021122
4	6676200.	0.014803
4	7020000.	0.015499
4	7363800.	0.015549
5	59400.	0.51034
5	232800.	0.804236
5	465600.	0.906523
5	640799.	0.963918
5	640802.	0.037232
5	809400.	0.28337
5	1760399.	0.521781
5	1760402.	0.015609
5	1950000.	0.185566
5	2095200.	0.232898
5	2265000.	0.234562
5	2438399.	0.248033
5	2610000.	0.087413
5	2784000.	0.104638
5	2931000.	0.110491
5	3128399.	0.112722
5	3301200.	0.039594
5	3474900.	0.048167
5	3646800.	0.05025
5	3822899.	0.051581
5	3992400.	0.029108
5	4182000.	0.032905
5	4342200.	0.033829
5	4513500.	0.033314
5	4686600.	0.033223
5	4856400.	0.033207
5	5043300.	0.032893
5	5981399.	0.0331
5	6330000.	0.012019
5	6676200.	0.01382
5	7020000.	0.011425
5	7363800.	0.015998

HWANG	TEST FOR	MSSFIT:vials	SMALL		
RKD	DEFF	DPATH	RLAM	XSS0	FAST

9.24	1.50E-08	0.1994	2	19.74	0
------	----------	--------	---	-------	---

"1 means fit parameter, 0 means keep it fixed"

0	1	0	0	1	0
---	---	---	---	---	---

"CONSTANTS(Ms,VLi," CLi)

6

1.9793	20.07863	0	11
1.9982	19.9397	0	9
2.0014	20.05824	0	12
2.0067	19.97104	0	12
1.9968	20.02191	0	31
2.0002	20.03113	0	31

1	59400.	0.565727	0.	0.
1	232800.	0.651193	0.	0.
1	465600.	0.636226	0.	0.
1	640800.	0.562581	0.	0.
1	809400.	0.645553	0.	0.
1	1760400.	0.440672	0.	0.
1	1950000.	0.875271	0.	0.
1	2095200.	0.535466	0.	0.
1	2438400.	0.697722	0.	0.
1	3128400.	0.72679	0.	0.
1	4182000.	0.680108	0.	0.
2	59400.	0.613232	0.	0.
2	232800.	0.568004	0.	0.
2	465600.	0.603688	0.	0.
2	640800.	0.595228	0.	0.
2	809400.	0.534816	0.	0.
2	1760400.	0.449458	0.	0.
2	1950000.	0.854881	0.	0.
2	2095200.	0.620499	0.	0.
2	2438400.	1.403471	0.	0.
3	59400.	0.725488	0.	0.
3	232800.	0.590889	0.	0.
3	465600.	0.522126	0.	0.
3	640800.	13.31558	15.19845	1.019145
3	640802.	0.525922	0.	0.
3	809400.	0.505206	0.	0.
3	1760400.	0.430043	0.	0.
3	1950000.	0.801518	0.	0.
3	2095200.	0.470933	0.	0.

3	2438400.	0.630586	0.	0.
3	3128400.	0.669924	0.	0.
3	4182000.	0.634078	0.	0.
4	59400.	0.656074	0.	0.
4	232800.	0.560087	0.	0.
4	465600.	0.596963	0.	0.
4	640800.	15.10832	16.83166	1.019145
4	640802.	0.568004	0.	0.
4	809400.	0.486443	0.	0.
4	1760400.	0.473427	0.	0.
4	1950000.	0.773427	0.	0.
4	2095200.	0.502278	0.	0.
4	2438400.	0.579284	0.	0.
4	3128400.	0.67487	0.	0.
4	4182000.	0.629696	0.	0.
5	59400.	0.580152	0.	0.
5	232800.	0.534599	0.	0.
5	465600.	0.618547	0.	0.
5	640800.	17.44761	20.02657	0.
5	640802.	0.43731	0.	0.
5	809400.	0.488069	0.	0.
5	1760400.	18.72148	18.71389	0.
5	1760402.	0.587419	0.	0.
5	1950000.	0.843492	0.	0.
5	2095200.	0.504447	0.	0.
5	2265000.	0.672885	0.	0.
5	2438400.	17.20293	20.07354	0.
5	2610000.	0.808503	0.	0.
5	2784000.	0.789436	0.	0.
5	2931000.	0.795369	0.	0.
5	3128400.	17.52201	19.99666	0.
5	3301200.	0.786692	0.	0.
5	3474900.	0.79679	0.	0.
5	3646800.	0.834707	0.	0.
5	3822900.	10.95003	12.95995	0.
5	3992400.	0.752256	0.	0.
5	4182000.	0.562494	0.	0.
5	4342200.	0.708774	0.	0.
5	4513500.	0.63872	0.	0.
5	4686600.	0.684371	0.	0.
5	4856400.	0.651735	0.	0.
5	5043300.	0.664273	0.	0.
5	5981400.	14.90602	20.06146	0.
5	6330000.	0.662375	0.	0.
5	6676200.	0.719935	0.	0.

5	7020000.	0.680412	0.	0.
6	59400.	0.572343	0.	0.
6	232800.	0.536551	0.	0.
6	465600.	0.586117	0.	0.
6	640800.	17.22417	19.10128	0.
6	640802.	0.511497	0.	0.
6	809400.	0.52115	0.	0.
6	1760400.	17.91237	18.77473	0.
6	1760402.	0.668004	0.	0.
6	1950000.	0.833189	0.	0.
6	2095200.	0.55141	0.	0.
6	2265000.	0.612907	0.	0.
6	2438400.	17.29588	20.03764	0.
6	2610000.	0.71513	0.	0.
6	2784000.	0.730423	0.	0.
6	2931000.	0.8032	0.	0.
6	3128400.	17.78042	20.31293	0.
6	3301200.	0.641269	0.	0.
6	3474900.	0.685716	0.	0.
6	3646800.	0.821627	0.	0.
6	3822900.	10.81356	13.05066	0.
6	3992400.	0.658286	0.	0.
6	4182000.	0.67808	0.	0.
6	4342200.	0.674837	0.	0.
6	4513500.	0.699555	0.	0.
6	4686600.	0.641399	0.	0.
6	4856400.	0.734024	0.	0.
6	5043300.	0.68205	0.	0.
6	5981400.	15.4524	20.0492	0.
6	6330000.	0.69923	0.	0.
6	6676200.	0.789273	0.	0.
6	7020000.	0.910531	0.	0.

1 0.001
EXP TIME(SECS) CONCENTRATION(CL)

1	59400.	0.547358
1	232800.	0.787202
1	465600.	0.840676
1	640800.	0.879067
1	809400.	0.886474
1	1760400.	0.898958
1	1950000.	0.869819
1	2095200.	0.86996
1	2438400.	0.907807

1	3128400.	0.893428
1	4182000.	0.882618
1	5981400.	0.857775
2	59400.	0.550653
2	232800.	0.785688
2	465600.	0.84032
2	640800.	0.87162
2	809400.	0.894537
2	1760400.	0.888209
2	1950000.	0.870991
2	2095200.	0.86481
2	2438400.	0.902122
2	3128400.	0.886992
3	59400.	0.539868
3	232800.	0.779709
3	465600.	0.833768
3	640799.	0.866186
3	640802.	0.98183
3	809400.	0.964973
3	1760400.	0.959851
3	1950000.	0.929249
3	2095200.	0.928593
3	2438400.	0.962273
3	3128400.	0.953907
3	4182000.	0.948398
3	5981400.	0.917977
4	59400.	0.536996
4	232800.	0.775193
4	465600.	0.831339
4	640799.	0.864649
4	640802.	0.995435
4	809400.	0.969826
4	1760400.	0.961226
4	1950000.	0.934943
4	2095200.	0.932012
4	2438400.	0.964918
4	3128400.	0.955553
4	4182000.	0.946171
4	5981400.	0.937504
5	59400.	0.552693
5	232800.	0.768155
5	465600.	0.830851
5	640799.	0.858701
5	640802.	0.034607
5	809400.	0.301257

5	1760399.	0.452246
5	1760402.	0.027694
5	1950000.	0.182129
5	2095200.	0.212369
5	2265000.	0.206301
5	2438399.	0.218111
5	2610000.	0.084838
5	2784000.	0.096567
5	2931000.	0.099367
5	3128399.	0.099156
5	3301200.	0.040456
5	3474900.	0.043837
5	3646800.	0.045115
5	3822899.	0.046924
5	3992400.	0.026926
5	4182000.	0.029182
5	4342200.	0.027974
5	4513500.	0.029221
5	4686600.	0.029473
5	4856400.	0.030127
5	5043300.	0.03018
5	5981399.	0.0285
5	6330000.	0.011756
5	6676200.	0.013301
5	7020000.	0.013202
5	7363800.	0.014454
6	59400.	0.533393
6	232800.	0.773172
6	465600.	0.837061
6	640799.	0.870789
6	640802.	0.047903
6	809400.	0.303824
6	1760399.	0.459906
6	1760402.	0.029101
6	1950000.	0.182679
6	2095200.	0.214011
6	2265000.	0.207006
6	2438399.	0.22045
6	2610000.	0.085549
6	2784000.	0.097685
6	2931000.	0.099889
6	3128399.	0.10049
6	3301200.	0.040994
6	3474900.	0.044085
6	3646800.	0.044664

6	3822899.	0.045154
6	3992400.	0.028818
6	4182000.	0.029445
6	4342200.	0.028988
6	4513500.	0.028668
6	4686600.	0.029446
6	4856400.	0.029394
6	5043300.	0.030887
6	5981399.	0.0283
6	6330000.	0.012685
6	6676200.	0.013535
6	7020000.	0.013669
6	7363800.	0.014495

HWANG TEST FOR MSSFIT:vials ALL-EVENLY MIXED

RKD DEFF DPATH RLAM XSS0 FAST

9.24 1.50E-08 0.22289 2 18.4199 0

"1 means fit parameter, 0 means keep it fixed"

0 0 1 1 0 0

"CONSTANTS(Ms,VLi," CLi)

10

1.9846 20.00922 0 11

2 20.07148 0 9

2.0002 20.09393 0 12

1.9874 20.0793 0 12

1.992 19.93113 0 12

1.986 20.036 0 12

1.9768 20.1001 0 31

1.9903 20.1543 0 31

1.9963 20.07256 0 35

1.9908 20.0732 0 35

1 59400. 0.617354 0. 0.

1 232800. 0.642191 0. 0.

1 465600. 0.533948 0. 0.

1 640800. 0.560737 0. 0.

1 809400. 0.462147 0. 0.

1 1760400. 0.546855 0. 0.

1 1950000. 0.99013 0. 0.

1 2095200. 0.661388 0. 0.

1 2438400. 0.640022 0. 0.

1 3128400. 0.727549 0. 0.

1 4182000. 0.656377 0. 0.

2 59400. 0.59848 0. 0.

2 232800. 0.56388 0. 0.

2 465600. 0.52993 0. 0.

2 640800. 0.580586 0. 0.

2 809400. 0.590239 0. 0.

2 1760400. 0.48102 0. 0.

2 1950000. 0.99132 0. 0.

2 2095200. 0.59273 0. 0.

2 2438400. 0.62386 0. 0.

3 59400. 0.530369 0. 0.

3 232800. 0.69013 0. 0.

3 465600. 0.635575 0. 0.

3 640800. 15.275 17.03286 0.

3	640801.	0.496746	0.	0.
3	809400.	0.621584	0.	0.
3	1760400.	0.453037	0.	0.
3	1950000.	0.730694	0.	0.
3	2095200.	0.569848	0.	0.
3	2438400.	0.683623	0.	0.
3	3128400.	0.695922	0.	0.
3	4182000.	0.670358	0.	0.
4	59400.	0.54859	0.	0.
4	232800.	0.55976	0.	0.
4	465600.	0.65108	0.	0.
4	640800.	16.6982	17.7255	0.
4	640801.	0.5077	0.	0.
4	809400.	0.47733	0.	0.
4	1760400.	0.52993	0.	0.
4	1950000.	0.640998	0.	0.
4	2095200.	0.55293	0.	0.
4	2438400.	0.56866	0.	0.
4	3128400.	0.70895	0.	0.
4	4182000.	0.72073	0.	0.
5	59400.	0.725488	0.	0.
5	232800.	0.601302	0.	0.
5	465600.	0.625922	0.	0.
5	640800.	15.91511	17.59255	1.019145
5	640801.	0.60564	0.	0.
5	809400.	0.495879	0.	0.
5	1760400.	0.481562	0.	0.
5	1950000.	0.814425	0.	0.
5	2095200.	0.446095	0.	0.
5	2438400.	0.622343	0.	0.
5	3128400.	0.782213	0.	0.
5	4182000.	0.616963	0.	0.
6	59400.	0.62907	0.	0.
6	232800.	0.52842	0.	0.
6	465600.	0.63623	0.	0.
6	640800.	15.3716	17.36864	1.019145
6	640801.	0.53059	0.	0.
6	809400.	0.5769	0.	0.
6	1760400.	0.41757	0.	0.
6	1950000.	0.69317	0.	0.
6	2095200.	0.42148	0.	0.
6	2438400.	0.59111	0.	0.
6	3128400.	0.71269	0.	0.
6	4182000.	0.674469	0.	0.
7	59400.	0.551193	0.	0.

7	232800.	0.61128	0.	0.
7	465600.	0.597505	0.	0.
7	640800.	17.18087	19.0839	0.
7	640801.	0.584599	0.	0.
7	809400.	0.495336	0.	0.
7	1760400.	18.19759	19.13805	0.
7	1760401.	0.61551	0.	0.
7	1950000.	0.860846	0.	0.
7	2095200.	0.490889	0.	0.
7	2265000.	0.72115	0.	0.
7	2438400.	17.35466	20.27831	0.
7	2610000.	0.735575	0.	0.
7	2784000.	0.820325	0.	0.
7	2931000.	0.753536	0.	0.
7	3128400.	17.76739	19.96565	0.
7	3301200.	0.838894	0.	0.
7	3474900.	0.811085	0.	0.
7	3646800.	0.808037	0.	0.
7	3822900.	10.11338	13.04502	0.
7	3992400.	0.737202	0.	0.
7	4182000.	0.606681	0.	0.
7	4342200.	0.764826	0.	0.
7	4513500.	0.627191	0.	0.
7	4686600.	0.676334	0.	0.
7	4856400.	0.729729	0.	0.
7	5043300.	0.654512	0.	0.
7	5981400.	15.62056	20.2224	0.
7	6330000.	0.749295	0.	0.
7	6676200.	0.750748	0.	0.
7	7020000.	0.593959	0.	0.
8	59400.	0.62928	0.	0.
8	232800.	0.58633	0.	0.
8	465600.	0.610195	0.	0.
8	640800.	17.29552	19.3881	0.
8	640801.	0.64035	0.	0.
8	809400.	0.51931	0.	0.
8	1760400.	18.4204	19.2242	0.
8	1760401.	0.60412	0.	0.
8	1950000.	0.864642	0.	0.
8	2095200.	0.608134	0.	0.
8	2265000.	0.76258	0.	0.
8	2438400.	17.1438	20.0534	0.
8	2610000.	0.80325	0.	0.
8	2784000.	0.78221	0.	0.
8	2931000.	0.82169	0.	0.

8	3128400.	17.43106	20.08453	0.
8	3301200.	0.859946	0.	0.
8	3474900.	0.734794	0.	0.
8	3646800.	0.79888	0.	0.
8	3822900.	12.5877	13.2212	0.
8	3992400.	0.85179	0.	0.
8	4182000.	0.578623	0.	0.
8	4342200.	0.755054	0.	0.
8	4513500.	0.74693	0.	0.
8	4686600.	0.58745	0.	0.
8	4856400.	0.69174	0.	0.
8	5043300.	0.61762	0.	0.
8	5981400.	13.5029	20.0997	0.
8	6330000.	0.660531	0.	0.
8	6676200.	0.82962	0.	0.
8	7020000.	0.86939	0.	0.
9	59400.	0.612039	0.	0.
9	232800.	0.57961	0.	0.
9	465600.	0.571692	0.	0.
9	640800.	18.7904	19.67337	1.019154
9	640801.	0.447072	0.	0.
9	809400.	0.470716	0.	0.
9	1760400.	18.7904	19.67337	1.019154
9	1760401.	0.534599	0.	0.
9	1950000.	0.736334	0.	0.
9	2095200.	0.475705	0.	0.
9	2265000.	0.586659	0.	0.
9	2438400.	17.59829	19.88625	1.019154
9	2610000.	0.741757	0.	0.
9	2784000.	0.644252	0.	0.
9	2931000.	0.833623	0.	0.
9	3128400.	17.46581	20.12351	0.
9	3301200.	0.73102	0.	0.
9	3474900.	0.692158	0.	0.
9	3646800.	0.764143	0.	0.
9	3822900.	17.87563	19.81885	1.019154
9	3992400.	0.64999	0.	0.
9	4182000.	0.70822	0.	0.
9	4342200.	0.65983	0.	0.
9	4513500.	17.7804	20.0405	0.
9	4686600.	0.62414	0.	0.
9	4856400.	0.645	0.	0.
9	5043300.	0.5842	0.	0.
9	5981400.	18.2824	20.1107	1.019154
9	6154200.	0.60509	0.	0.

9	6330000.	0.70331	0.	0.
9	6499800.	0.72995	0.	0.
9	6676200.	17.9883	20.1603	0.
9	6849000.	0.74768	0.	0.
9	7020000.	0.77612	0.	0.
9	7189200.	0.82286	0.	0.
10	59400.	0.71876	0.	0.
10	232800.	0.588612	0.	0.
10	465600.	0.62484	0.	0.
10	640800.	18.6521	19.5206	1.019154
10	640801.	0.52993	0.	0.
10	809400.	0.51714	0.	0.
10	1760400.	18.6521	19.5206	1.019154
10	1760401.	0.54089	0.	0.
10	1950000.	0.82375	0.	0.
10	2095200.	0.50488	0.	0.
10	2265000.	0.64577	0.	0.
10	2438400.	17.4717	20.0867	1.019154
10	2610000.	0.72679	0.	0.
10	2784000.	0.68232	0.	0.
10	2931000.	0.71768	0.	0.
10	3128400.	17.79	9.9214	0.
10	3301200.	0.82636	0.	0.
10	3474900.	0.82689	0.	0.
10	3646800.	0.82569	0.	0.
10	3822900.	17.3265	19.9664	1.019154
10	3992400.	0.66908	0.	0.
10	4182000.	0.71772	0.	0.
10	4342200.	0.64759	0.	0.
10	4513500.	17.9862	20.0824	0.
10	4686600.	0.55777	0.	0.
10	4856400.	0.61991	0.	0.
10	5043300.	0.64191	0.	0.
10	5981400.	18.3442	20.1017	1.019154
10	6154200.	0.61348	0.	0.
10	6330000.	0.75258	0.	0.
10	6499800.	0.7142	0.	0.
10	6676200.	18.0075	20.0621	0.
10	6849000.	0.93619	0.	0.
10	7020000.	0.78196	0.	0.
10	7189200.	0.88274	0.	0.

1 0.001
EXP TIME(SECS) CONCENTRATION(CL)

1	59400.	0.489271
1	232800.	0.784619
1	465600.	0.866427
1	640800.	0.92204
1	809400.	0.946664
1	1760400.	0.977855
1	1950000.	0.947437
1	2095200.	0.933902
1	2438400.	0.900912
1	3128400.	0.97782
1	4182000.	0.963212
1	5981400.	0.940784
2	59400.	0.4892
2	232800.	0.77656
2	465600.	0.86292
2	640800.	0.920127
2	809400.	0.950984
2	1760400.	0.9762
2	1950000.	0.94734
2	2095200.	0.9481
2	2438400.	0.9863
2	3128400.	0.97402
3	59400.	0.485888
3	232800.	0.77593
3	465600.	0.861416
3	640799.	0.920392
3	640802.	0.136394
3	809400.	0.35956
3	1760400.	0.55947
3	1950000.	0.555556
3	2095200.	0.544929
3	2438400.	0.570498
3	3128400.	0.566607
3	4182000.	0.560518
3	5981400.	0.560387
4	59400.	0.49116
4	232800.	0.7818
4	465600.	0.8669
4	640799.	0.9259
4	640802.	0.0776
4	809400.	0.3153
4	1760400.	0.5313
4	1950000.	0.51889
4	2095200.	0.5157
4	2438400.	0.5411

4	3128400.	0.5369
4	4182000.	0.5343
4	5981400.	0.5204
5	59400.	0.515262
5	232800.	0.799682
5	465600.	0.896983
5	640799.	0.939586
5	640801.	0.010794
5	809400.	0.011874
5	1760400.	0.011883
5	1950000.	0.996119
5	2095200.	0.999712
5	2438400.	1.033854
5	3128400.	1.030237
5	4182000.	1.016842
5	5981400.	0.986695
6	59400.	0.46451
6	232800.	0.77577
6	465600.	0.86985
6	640799.	0.92288
6	640801.	1.00549
6	809400.	1.00301
6	1760400.	1.00977
6	1950000.	0.98787
6	2095200.	0.99434
6	2438400.	1.03064
6	3128400.	1.02535
6	4182000.	1.017624
6	5981400.	0.98727
7	59400.	0.51747
7	232800.	0.778864
7	465600.	0.86582
7	640799.	0.918079
7	640802.	0.052576
7	809400.	0.286223
7	1760399.	0.504229
7	1760402.	0.02422
7	1950000.	0.18502
7	2095200.	0.22581
7	2265000.	0.22696
7	2438399.	0.243079
7	2610000.	0.086465
7	2784000.	0.104149
7	2931000.	0.11002
7	3128399.	0.11363

7	3301200.	0.04152
7	3474900.	0.04897
7	3646800.	0.053012
7	3822899.	0.052947
7	3992400.	0.031045
7	4182000.	0.033379
7	4342200.	0.032656
7	4513500.	0.033983
7	4686600.	0.036206
7	4856400.	0.034817
7	5043300.	0.036197
7	5981399.	0.0336
7	6330000.	0.01405
7	6676200.	0.015076
7	7020000.	0.015749
7	7363800.	0.015791
8	59400.	0.52401
8	232800.	0.79575
8	465600.	0.890037
8	640799.	0.932678
8	640802.	0.04718
8	809400.	0.28457
8	1760399.	0.50546
8	1760402.	0.02119
8	1950000.	0.187118
8	2095200.	0.227571
8	2265000.	0.22615
8	2438399.	0.2434
8	2610000.	0.08841
8	2784000.	0.10732
8	2931000.	0.11317
8	3128399.	0.113115
8	3301200.	0.042849
8	3474900.	0.049517
8	3646800.	0.05393
8	3822899.	0.05382
8	3992400.	0.03021
8	4182000.	0.033736
8	4342200.	0.033432
8	4513500.	0.03375
8	4686600.	0.03371
8	4856400.	0.03471
8	5043300.	0.0358
8	5981399.	0.03323
8	6330000.	0.01555

8	6676200.	0.015586
8	7020000.	0.01616
8	7363800.	0.01755
9	59400.	0.501306
9	232800.	0.791117
9	465600.	0.882751
9	640799.	1.038473
9	640802.	1.018186
9	809400.	1.01164
9	1760399.	1.038473
9	1760402.	1.019473
9	1950000.	1.036177
9	2095200.	1.041447
9	2265000.	1.027875
9	2438399.	1.04409
9	2610000.	1.032939
9	2784000.	1.033579
9	2931000.	1.032649
9	3128399.	1.033401
9	3301200.	0.403339
9	3474900.	0.463731
9	3646800.	0.485141
9	3822899.	0.494254
9	3992400.	0.81473
9	4182000.	0.77997
9	4342200.	0.77234
9	4513499.	0.76263
9	4686600.	0.02862
9	4856400.	0.32863
9	5043300.	0.34978
9	5981399.	0.36055
9	6154200.	0.80478
9	6330000.	0.745
9	6499800.	0.722
9	6676199.	0.71663
9	6849000.	0.25722
9	7020000.	0.30926
9	7189200.	0.32505
9	7363800.	0.32752
10	59400.	0.49732
10	232800.	0.780874
10	465600.	0.87641
10	640799.	1.04271
10	640802.	1.01788
10	809400.	1.02162

10	1760399.	1.04271
10	1760402.	1.01975
10	1950000.	1.03854
10	2095200.	1.04442
10	2265000.	1.032402
10	2438399.	1.04897
10	2610000.	1.03214
10	2784000.	1.03928
10	2931000.	1.03415
10	3128399.	1.03302
10	3301200.	0.39494
10	3474900.	0.46041
10	3646800.	0.48413
10	3822899.	0.49126
10	3992400.	0.8217
10	4182000.	0.78951
10	4342200.	0.77691
10	4513499.	0.76548
10	4686600.	0.02761
10	4856400.	0.32353
10	5043300.	0.34467
10	5981399.	0.35533
10	6154200.	0.8063
10	6330000.	0.74943
10	6499800.	0.7282
10	6676199.	0.72041
10	6849000.	0.25208
10	7020000.	0.30649
10	7189200.	0.32178
10	7363800.	0.32648

HWANG TEST FOR MSSFIT:vials ALL-NON-EVENLY MIXED

RKD DEFF DPATH RLAM XSS0 FAST

9.24 1.50E-08 0.22289 2 7.86985 0

"1 means fit parameter, 0 means keep it fixed"

0 0 1 1 0 0

"CONSTANTS(Ms,VLi," CLi)

10

1.9884 19.86171 0 11

1.986 20.011 0 11

1.9907 20.00412 0 12

1.9799 20.01822 0 12

2.0132 20.15499 0 12

1.9012 20.0236 0 12

2.0025 20.17397 0 31

2.0028 20.0303 0 31

1.9926 20.0898 0 35

1.9937 19.9588 0 35

1 59400. 0.631996 0. 0.

1 232800. 0.612581 0. 0.

1 465600. 0.614751 0. 0.

1 640800. 0.674946 0. 0.

1 809400. 0.663015 0. 0.

1 1760400. 0.497614 0. 0.

1 1950000. 0.922668 0. 0.

1 2095200. 0.583406 0. 0.

1 2438400. 0.627549 0. 0.

1 3128400. 0.692408 0. 0.

1 4182000. 0.727332 0. 0.

2 59400. 0.6145 0. 0.

2 232800. 0.556 0. 0.

2 465600. 0.5466 0. 0.

2 640800. 0.60239 0. 0.

2 809400. 0.619306 0. 0.

2 1760400. 0.5126 0. 0.

2 1950000. 0.9322 0. 0.

2 2095200. 0.6133 0. 0.

2 2438400. 0.6383 0. 0.

2 3128400. 0.8014 0. 0.

2 4182000. 0.7396 0. 0.

3 59400. 0.584056 0. 0.

3 232800. 0.624187 0. 0.

3	465600.	0.6359	0.	0.
3	640800.	14.9	17.02164	0
3	640801.	1.375488	0.	0.
3	809400.	0.451735	0.	0.
3	1760400.	0.50564	0.	0.
3	1950000.	0.68308	0.	0.
3	2095200.	0.547831	0.	0.
3	2438400.	0.464534	0.	0.
3	3128400.	0.696855	0.	0.
3	4182000.	0.695304	0.	0.
4	59400.	0.570824	0.	0.
4	232800.	0.55922	0.	0.
4	465600.	0.64165	0.	0.
4	640800.	15.3686	17.1083	0.
4	640801.	1.25607	0.	0.
4	809400.	0.46215	0.	0.
4	1760400.	0.42462	0.	0.
4	1950000.	0.787527	0.	0.
4	2095200.	0.51432	0.	0.
4	2438400.	0.52657	0.	0.
4	3128400.	0.8038	0.	0.
4	4182000.	0.71559	0.	0.
5	59400.	0.716377	0.	0.
5	232800.	0.573536	0.	0.
5	465600.	0.571367	0.	0.
5	640800.	13.74919	15.52436	1.019145
5	640801.	0.521475	0.	0.
5	809400.	0.626681	0.	0.
5	1760400.	0.403471	0.	0.
5	1950000.	0.845336	0.	0.
5	2095200.	0.502169	0.	0.
5	2438400.	0.591106	0.	0.
5	3128400.	0.780694	0.	0.
5	4182000.	0.718384	0.	0.
6	59400.	0.66106	0.	0.
6	232800.	0.55662	0.	0.
6	465600.	0.58004	0.	0.
6	640800.	15.1847	16.75641	1.019145
6	640801.	0.54002	0.	0.
6	809400.	0.50803	0.	0.
6	1760400.	0.40087	0.	0.
6	1950000.	0.57668	0.	0.
6	2095200.	0.55846	0.	0.
6	2438400.	0.6192	0.	0.
6	3128400.	0.7039	0.	0.

6	4182000.	0.636486	0.	0.
7	59400.	0.638612	0.	0.
7	232800.	0.489805	0.	0.
7	465600.	0.640889	0.	0.
7	640800.	17.3663	19.25795	0.
7	640801.	0.540564	0.	0.
7	809400.	0.54154	0.	0.
7	1760400.	18.43679	19.34775	0.
7	1760401.	0.627115	0.	0.
7	1950000.	0.880152	0.	0.
7	2095200.	0.559436	0.	0.
7	2265000.	0.702603	0.	0.
7	2438400.	17.25336	20.04187	0.
7	2610000.	0.830694	0.	0.
7	2784000.	0.776139	0.	0.
7	2931000.	0.827679	0.	0.
7	3128400.	17.43715	20.08735	0.
7	3301200.	0.775076	0.	0.
7	3474900.	0.840282	0.	0.
7	3646800.	0.855868	0.	0.
7	3822900.	10.69758	12.96563	0.
7	3992400.	0.747213	0.	0.
7	4182000.	0.667798	0.	0.
7	4342200.	0.665173	0.	0.
7	4513500.	0.758482	0.	0.
7	4686600.	0.750911	0.	0.
7	4856400.	0.646161	0.	0.
7	5043300.	0.685738	0.	0.
7	5981400.	14.91734	20.09642	0.
7	6330000.	0.74753	0.	0.
7	6676200.	0.8586	0.	0.
7	7020000.	0.797538	0.	0.
8	59400.	0.61844	0.	0.
8	232800.	0.61041	0.	0.
8	465600.	0.566703	0.	0.
8	640800.	17.32593	19.2143	0.
8	640801.	0.54273	0.	0.
8	809400.	0.4333	0.	0.
8	1760400.	18.230	19.2272	0.
8	1760401.	0.64859	0.	0.
8	1950000.	0.935683	0.	0.
8	2095200.	0.630694	0.	0.
8	2265000.	0.76985	0.	0.
8	2438400.	17.0445	19.9116	0.
8	2610000.	0.78178	0.	0.

8	2784000.	0.86453	0.	0.
8	2931000.	0.39523	0.	0.
8	3128400.	17.7567	20.077	0.
8	3301200.	0.768839	0.	0.
8	3474900.	0.767961	0.	0.
8	3646800.	0.84604	0.	0.
8	3822900.	11.8193	12.9883	0.
8	3992400.	0.66374	0.	0.
8	4182000.	0.686236	0.	0.
8	4342200.	0.700846	0.	0.
8	4513500.	0.63892	0.	0.
8	4686600.	0.66632	0.	0.
8	4856400.	0.68132	0.	0.
8	5043300.	0.62524	0.	0.
8	5981400.	14.149	20.0679	0.
8	6330000.	0.771367	0.	0.
8	6676200.	0.799642	0.	0.
8	7020000.	0.89508	0.	0.
9	59400.	0.579393	0.	0.
9	232800.	0.559653	0.	0.
9	465600.	0.608351	0.	0.
9	640800.	18.8921	20.08321	1.019154
9	640801.	0.484924	0.	0.
9	809400.	0.435033	0.	0.
9	1760400.	18.8921	20.08321	1.019154
9	1760401.	0.489262	0.	0.
9	1950000.	0.807267	0.	0.
9	2095200.	0.580803	0.	0.
9	2265000.	0.586876	0.	0.
9	2438400.	18.18926	19.96139	1.019154
9	2610000.	0.666161	0.	0.
9	2784000.	0.748482	0.	0.
9	2931000.	0.759328	0.	0.
9	3128400.	17.63196	20.03912	0.
9	3301200.	0.736226	0.	0.
9	3474900.	0.802603	0.	0.
9	3646800.	0.771204	0.	0.
9	3822900.	17.66934	19.89665	1.019154
9	3992400.	0.62273	0.	0.
9	4182000.	0.72161	0.	0.
9	4342200.	0.58133	0.	0.
9	4513500.	17.8965	20.1091	0.
9	4686600.	0.67597	0.	0.
9	4856400.	0.71169	0.	0.
9	5043300.	0.65755	0.	0.

9	5981400.	18.1031	19.9279	1.019154
9	6154200.	0.57921	0.	0.
9	6330000.	0.70055	0.	0.
9	6499800.	0.71283	0.	0.
9	6676200.	17.9606	19.9655	0.
9	6849000.	0.84709	0.	0.
9	7020000.	0.83477	0.	0.
9	7189200.	0.91732	0.	0.
10	59400.	0.59393	0.	0.
10	232800.	0.535358	0.	0.
10	465600.	0.618	0.	0.
10	640800.	18.5663	19.5912	1.019154
10	640801.	0.50022	0.	0.
10	809400.	0.44783	0.	0.
10	1760400.	18.5663	19.5912	1.019154
10	1760401.	0.58254	0.	0.
10	1950000.	0.81746	0.	0.
10	2095200.	0.55195	0.	0.
10	2265000.	0.632321	0.	0.
10	2438400.	17.3636	20.0335	1.019154
10	2610000.	0.80607	0.	0.
10	2784000.	0.64555	0.	0.
10	2931000.	0.66106	0.	0.
10	3128400.	17.6918	20.0976	0.
10	3301200.	0.93941	0.	0.
10	3474900.	0.87123	0.	0.
10	3646800.	0.68155	0.	0.
10	3822900.	17.6204	20.1098	1.019154
10	3992400.	0.81677	0.	0.
10	4182000.	0.62413	0.	0.
10	4342200.	0.68508	0.	0.
10	4513500.	17.9006	20.0311	0.
10	4686600.	0.60004	0.	0.
10	4856400.	0.65993	0.	0.
10	5043300.	0.6321	0.	0.
10	5981400.	18.2166	20.0587	1.019154
10	6154200.	0.58996	0.	0.
10	6330000.	0.64973	0.	0.
10	6499800.	0.77182	0.	0.
10	6676200.	18.0614	20.0561	0.
10	6849000.	0.77948	0.	0.
10	7020000.	0.77916	0.	0.
10	7189200.	0.85995	0.	0.

1 0.001
EXP TIME(SECS) CONCENTRATION(CL)

1	59400	0.526259
1	232800	0.80049
1	465600	0.86858
1	640800	0.910767
1	809400	0.933577
1	1760400	0.954606
1	1950000	0.923559
1	2095200	0.924812
1	2438400	0.959552
1	3128400	0.946662
1	4182000	0.938791
1	5981400	0.910108
2	59400	0.52584
2	232800	0.798979
2	465600	0.8685
2	640800	0.908355
2	809400	0.929375
2	1760400	0.95024
2	1950000	0.9199
2	2095200	0.91563
2	2438400	0.95685
2	3128400	0.94111
2	4182000	0.93642
2	5981400	0.90294
3	59400	0.522844
3	232800	0.8044
3	465600	0.878518
3	640799	0.925078
3	640802	0.148712
3	809400	0.378655
3	1760400	0.553296
3	1950000	0.523009
3	2095200	0.534516
3	2438400	0.559203
3	3128400	0.554977
3	4182000	0.555578
3	5981400	0.533624
4	59400	0.51497
4	232800	0.7904
4	465600	0.8629
4	640799	0.9158
4	640802	0.1319

4	809400	0.3703
4	1760400	0.5433
4	1950000	0.51557
4	2095200	0.5264
4	2438400	0.5497
4	3128400	0.545
4	4182000	0.5427
4	5981400	0.5264
5	59400	0.529992
5	232800	0.805178
5	465600	0.883274
5	640799	0.919884
5	640801	0.996668
5	809400	0.99364
5	1760400	0.990835
5	1950000	0.966819
5	2095200	0.97354
5	2438400	1.006532
5	3128400	0.996616
5	4182000	0.981465
5	5981400	0.958198
6	59400	0.50462
6	232800	0.78707
6	465600	0.86529
6	640799	0.90603
6	640801	1.00177
6	809400	0.98694
6	1760400	0.98411
6	1950000	0.96404
6	2095200	0.96429
6	2438400	0.99965
6	3128400	0.98959
6	4182000	0.976394
6	5981400	0.95407
7	59400	0.521502
7	232800	0.800043
7	465600	0.887644
7	640799	0.918555
7	640802	0.046993
7	809400	0.286625
7	1760399	0.491475
7	1760402	0.018985
7	1950000	0.1897
7	2095200	0.224909
7	2265000	0.223562

7	2438399	0.234936
7	2610000	0.088149
7	2784000	0.105013
7	2931000	0.109544
7	3128399	0.109297
7	3301200	0.043185
7	3474900	0.048711
7	3646800	0.05042
7	3822899	0.052195
7	3992400	0.030202
7	4182000	0.032349
7	4342200	0.03404
7	4513500	0.032708
7	4686600	0.035063
7	4856400	0.033065
7	5043300	0.034685
7	5981399	0.0322
7	6330000	0.016316
7	6676200	0.014771
7	7020000	0.015537
7	7363800	0.016717
8	59400	0.52446
8	232800	0.82009
8	465600	0.890939
8	640799	0.925488
8	640802	0.0418
8	809400	0.29162
8	1760399	0.4913
8	1760402	0.02235
8	1950000	0.188993
8	2095200	0.225257
8	2265000	0.22189
8	2438399	0.23583
8	2610000	0.0915
8	2784000	0.10508
8	2931000	0.10953
8	3128399	0.110358
8	3301200	0.042328
8	3474900	0.048209
8	3646800	0.05244
8	3822899	0.05189
8	3992400	0.03028
8	4182000	0.032815
8	4342200	0.032945
8	4513500	0.03274

8	4686600	0.03161
8	4856400	0.0325
8	5043300	0.03424
8	5981399	0.0335
8	6330000	0.013855
8	6676200	0.015535
8	7020000	0.014361
8	7363800	0.01693
9	59400	0.511143
9	232800	0.805351
9	465600	0.877419
9	640799	1.02469
9	640802	1.017245
9	809400	1.015486
9	1760399	1.027469
9	1760402	1.019404
9	1950000	1.029391
9	2095200	1.032993
9	2265000	1.019936
9	2438399	1.039962
9	2610000	1.030744
9	2784000	1.029509
9	2931000	1.028057
9	3128399	1.026596
9	3301200	0.410319
9	3474900	0.469812
9	3646800	0.490139
9	3822899	0.496918
9	3992400	0.81257
9	4182000	0.77874
9	4342200	0.77093
9	4513499	0.75963
9	4686600	0.02894
9	4856400	0.33233
9	5043300	0.3561
9	5981399	0.36021
9	6154200	0.79961
9	6330000	0.73736
9	6499800	0.7174
9	6676199	0.71108
9	6849000	0.26115
9	7020000	0.31567
9	7189200	0.33165
9	7363800	0.3305
10	59400	0.5119

10	232800	0.8
10	465600	0.88436
10	640799	1.01945
10	640802	1.0181
10	809400	1.01433
10	1760399	1.01945
10	1760402	1.01915
10	1950000	1.02791
10	2095200	1.03223
10	2265000	1.01773
10	2438399	1.0363
10	2610000	1.03347
10	2784000	1.03305
10	2931000	1.03228
10	3128399	1.02419
10	3301200	0.40391
10	3474900	0.46781
10	3646800	0.48731
10	3822899	0.49351
10	3992400	0.8159
10	4182000	0.78186
10	4342200	0.7741
10	4513499	0.7623
10	4686600	0.02912
10	4856400	0.34099
10	5043300	0.35867
10	5981399	0.3674
10	6154200	0.79511
10	6330000	0.737
10	6499800	0.71527
10	6676199	0.71191
10	6849000	0.25974
10	7020000	0.31281
10	7189200	0.32921
10	7363800	0.32685

MSS Model Code

File Name: Fitmssbm.for

```
C
C Program Testfit
C
C Adapted for batch system experiencing:
C   Multisite (series) sorption on soil (variable distribution)
C   Liquid-phase added/removed perturbations
C   Simultaneous Fitting multiple experiments
C
C NUMERICAL SOLUTION
C
C BY: E. Heyse and D.C. Coulliette
C University of Florida, 13 Feb 97
C
C
C dim scrat = 5*np + np*np +(2+np)*nob
C signs = 1 means parms cannot change sign
C P(IPOINT(I)) = VAL(I) == PNAME(I)
C
C IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C   DOUBLE PRECISION RKD,DEFF,DPATH,RLAM,XSS0,FAST
C   DOUBLE PRECISION XM(10),V(10),PC0(10),XEFT(10),TF
C   DOUBLE PRECISION TBCC(220),VR(220),VA(220),CA(220)
C   DOUBLE PRECISION XMR,XKPR,XKR,XFR,XSR0
C   DOUBLE PRECISION X(250)
C   DIMENSION IX(250),Y(250),P(7),DIFF(7),SIGNS(7),SCRAT(1999)
C   DIMENSION IFC(220),NEFD(10)
C   CHARACTER*8 PNAME(7)
C   CHARACTER*15 INFIL,OUT1,OUT2
C   DIMENSION VAL(7),IPOINT(7),IVARY(7)
C   COMMON /BMOD/XM,V,PC0,XEFT,NEFD,TBCC,VR,VA,CA
C   COMMON /BMODA/XMR,XKPR,XKR,XFR,IFLAG,TF
C   COMMON /VALUE/ VAL,IPOINT,IVARY,PNAME,NFIX
C   COMMON /BDAT/ IX,X,NEXP
C   CHARACTER*80 TIT,LIN1,LIN2,LIN3,LIN4
C   NFIX=6
C   PNAME(1)=' Kd '
C   PNAME(2)=' Deff '
C   PNAME(3)=' dpath '
C   PNAME(4)=' Lambda '
C   PNAME(5)=' Ss0 '
C   PNAME(6)=' Fast '
```

```

WRITE(*,*) 'NAME OF INPUT FILE?'
READ(5,1111)INFIL
1111 FORMAT(A15)
WRITE(6,*)'NAME OF SHORT OUTPUT FILE?'
READ(5,1111)OUT1
WRITE(6,*)'NAME OF LONG OUTPUT FILE?'
READ(5,1111)OUT2
OPEN(UNIT=3,FILE=INFIL,STATUS='OLD')
OPEN(UNIT=10,FILE=OUT1,STATUS='NEW')
OPEN(UNIT=4,FILE=OUT2,STATUS='NEW')
READ(3,'(A)') TIT
C
C   Read parameters to be fitted
C
C   RKD = partition coefficient, KP,
C   DEFF = Coefficient of Diffusion, D_eff cm^2/sec
C   DPATH = Total diff. path length, d, cm
C   RLAM = shape factor Lambda
C   XSS0 = Initial dmIs Concentration in slow soil sites, Sso, ug/g
C   FAST = Fraction of equilibrium sorption sites
C
C   READ(3,'(A)') LIN1
C   READ(3,*) RKD,DEFF,DPATH,RLAM,XSS0,FAST
C
C   Read Constants
C
C   FOC = Mass fraction organic carbon on soil, foc
C   XM = Mass of soil in reactor, g
C   V = Volume of solvent in reactor at time zero, mL
C   PC0 = initial concentration in liquid, mg/l
C   NEFD = Number of boundary condition changes
C   IFC = boundary condition number
C   TBCC = time for boundary condition to end
C   XQ = Flow rate, mL/min
C   XCIN = Dimensionless inlet concentration
C   XMR = Mass of reactor, g
C   XKPR = Linear partition coef. on reactor, mL/g
C   XKR = 1st order mass transfer rate onto reactor, min^-1
C   XFR = Fraction instantaneous sorbing reactor sites
C   VS(J) = volume of liquid in rx for BC period j, ml
C   VR(J) = volume of liquid removed at end of BC period J, ml.
C   VA(j) = volume of liquid added at end of BC period J, ml.
C   CA(J) = concentration in liquid added at end of BC period J,mg/l.
C   XIC = sorbed concentration in each slow compartment, ug/g
C   CL = current liquid concentration, mg/l

```

```

C
  READ(3,'(A)') LIN2
  READ(3,*) (IVARY(I),I=1,NFIX)
  READ(3,'(A)') LIN3
  READ(3,*)NEXP
  NABC=0
  DO 17 I=1,NEXP
    READ(3,*) XM(I),V(I),PC0(I),NEFD(I)
C    READ(3,*) XMR,XKPR,XKR,XFR
    NABC=NABC+NEFD(I)
  17 CONTINUE
    DO 6 I=1,NABC
      6 READ(3,*) IFC(I),TBCC(I),VR(I),VA(I),CA(I)
C    Read numerical parameter
C    IFLAG=0 for sorbed/liquid concentration
C    IFLAG=1 for liquid concentration
c    TF = time factor = time of time step/time for mass transfer
c    Try TF = 0.01
    READ(3,*) IFLAG, TF
C
C    Read Data to be fitted
C
C    X = time, seconds
C    Y = observation at time X, see IFLAG.
c
c    XEFT(I) = experiment final time (last observation for each exp.
c
C
  READ(3,'(A)') LIN4
  NOB=0
  DO 3 I=1,200
    READ(3,*,END=4) IX(I),X(I),Y(I)
    IF ((I.GE.2).AND.(IX(I).NE.IX(I-1))) XEFT(IX(I-1))=X(I-1)
  3  NOB=NOB+1
  4  WRITE(4,1) TIT
    XEFT(NEXP)=X(NOB)
  1  FORMAT(' ',A)
    WRITE(4,1) LIN1
    WRITE(4,2) RKD,DEFF,DPATH,RLAM,XSS0,FAST
  2  FORMAT(' ',7E12.6)
    WRITE(4,1) LIN2
    WRITE(4,5) (IVARY(I),I=1,NFIX)
  5  FORMAT(' ',7I10)
    WRITE(4,1) LIN3
    DO 18 I=1,NEXP

```

```

        WRITE(4,777) XM(I),V(I),PC0(I),XEFT(I),NEFD(I)
18  CONTINUE
777  FORMAT(' ',(4E12.6,/),I10)
        DO 778 I=1,NABC
            WRITE(4,779) IFC(I),TBCC(I),VR(I),VA(I),CA(I)
778  CONTINUE
779  FORMAT(' ',I10,4E12.6)
        VAL(1)=RKD
        VAL(2)=DEFF
        VAL(3)=DPATH
        VAL(4)=RLAM
        VAL(5)=XSS0
        VAL(6)=FAST
        NP=0
        JFIX=NFIX
        DO 20 I=1,NFIX
            IF (IVARY(I).EQ.1) THEN
                NP=NP+1
                IPOINT(I)=NP
            ELSE
                IPOINT(I)=JFIX
                JFIX=JFIX-1
            ENDIF
20  CONTINUE
        DO 22 I=1,NFIX
            P(IPOINT(I))=VAL(I)
22  CONTINUE
        NPROB=1
        MIT=0
        EPS1=0.0
        EPS2=0.0
        FLAM=0.0
        IF(EPS1.LT.1.E-9) EPS1=0.0
        IF(EPS2.LT.1.E-9) EPS2=1.E-3
        IF(MIT.EQ.0) MIT=15
        IF(FLAM.LT.1.E-9) FLAM=0.01
        FNU=10.
        DO 9 I=1,6
            SIGNS(I)=1.0
9  DIFF(I)=0.01
        WRITE(4,7) NPROB
7  FORMAT(' PROBLEM NUMBER',I3,T26,'X',T38,'Y'/)
        WRITE(4,8) (X(I),Y(I),I=1,NOB)
8  FORMAT(' ',T19,2E12.5)
        WRITE(*,12) (PNAME(I),I=1,NFIX)

```



```

WRITE(10,12) (PNAME(I),I=1,NFIX)
12  FORMAT(/T6,'SSQ',T11,7A12)
WRITE(*,15) (P(IPOINT(I)),I=1,NFIX)
WRITE(10,15) (P(IPOINT(I)),I=1,NFIX)
15  FORMAT(T11,7E12.5)
CALL UWHAUS(NPROB,NOB,Y,NP,P,DIFF,SIGNS,EPS1,EPS2,MIT,FLAM,
*FNU,SCRAT)
WRITE(*,14) TIT
WRITE(10,14) TIT
14  FORMAT(' END: ',A)
999 STOP
END

```

```

SUBROUTINE UWHAUS(NPROB,NOB,Y,NP,TH,DIFF,SIGNS,EPS1,EPS2,
1 MIT, FLAM, FNU, SCRAT)
DIMENSION SCRAT(1),Y(1),TH(1),DIFF(1),SIGNS(1)
IA=1
IB=IA+NP
IC=IB+NP
ID=IC+NP
IE=ID+NP
IF=IE+NP
IG=IF+NOB
IH=IG+NOB
II = IH + NP * NOB
IJ = IH

```

```

CALL HAUS59(NPROB,NOB,Y,NP,TH,DIFF,SIGNS,EPS1,EPS2,MIT
1 ,FLAM,FNU,SCRAT(IA), SCRAT(IB), SCRAT(IC), SCRAT(ID),
2 SCRAT(IE), SCRAT(IF), SCRAT(IG), SCRAT(IH), SCRAT(II),
3 SCRAT(IJ) )
RETURN
END

```

```

SUBROUTINE HAUS59(NPRBO, NBO, Y,NQ,TH,DIFZ,SIGNS,EP1S,EP2S,
1MIT,FLAM,FNU, Q,P,E,PHI,TB,F,R,A,D,DELZ)
DIMENSION TH(1), DIFZ(1), SIGNS(1), Y(1), Q(1), P(1), E(1),
1 PHI(1), TB(1), F(1), R(1), A(1), D(1), DELZ(1)
CHARACTER*8 PNAME(7)
DIMENSION VAL(7),IPOINT(7),IVARY(7)
COMMON /VALUE/ VAL,IPOINT,IVARY,PNAME,NFIX
DATA MAXCNT/6/
ACOS(X) = ATAN(SQRT(1.0/X**2 - 1.0))
NP = NQ
NPROB = NPRBO
NOB = NBO
EPS1 = EP1S

```

```

EPS2 = EP2S
NPSQ = NP * NP
NSCRAC = 5*NP+NPSQ +2*NOB+NP*NOB
WRITE(4, 1000) NPROB, NOB, NP, NSCRAC
WRITE(4, 1001)
CALL GASS60(1, NP, TH, TEMP, TMEP)
WRITE(4, 1002)
CALL GASS60(1, NP, DIFZ, TEMP, TEMP)
IF(MIN0(NP-1,50-NP,NOB-NP,MIT-1,999-MIT))99,15,15
15 IF(FNU-1.0)99, 99, 16
16 CONTINUE
DO 19 I=1,NP
TEMP = ABS(DIFZ(I))
IF(AMIN1(1.0-TEMP, ABS(TH(I))))99, 99, 19
19 CONTINUE
GA = FLAM
NIT = 1
ASSIGN 131 TO LAOS
ASSIGN 225 TO IRAN
ASSIGN 265 TO JORDAN
IF(EPS1) 5, 10, 10
5 EPS1 = 0
10 IF(EPS2) 40, 40, 30
40 IF(EPS1) 60, 60, 50
60 ASSIGN 270 TO IRAN
GO TO 70
50 ASSIGN 265 TO IRAN
GO TO 70
30 IF(EPS1) 80, 80, 70
80 ASSIGN 270 TO JORDAN
70 SSQ = 0
DO 71 I=1,NFIX
IF(IVARY(I).EQ.1) VAL(I)=TH(IPOINT(I))
71 CONTINUE
CALL MODEL(NPROB, TH, F, NOB, NP)
DO 90 I = 1, NOB
R(I) = Y(I) - F(I)
90 SSQ=SSQ+R(I)*R(I)
WRITE(4, 1003) SSQ
WRITE(*,3003) SSQ,(TH(IPOINT(I)),I=1,NFIX)
WRITE(10,3003) SSQ,(TH(IPOINT(I)),I=1,NFIX)
3003 FORMAT(' ',1PE9.2,0P7E12.5)
WRITE(4, 1011)
WRITE(4, 2006) (F(I),I=1,NOB)
C BEGIN ITERATION

```

```

100 GA = GA / FNU
    INTCNT = 0
    WRITE(4, 1004) NIT
101 JS = 1 - NOB
    DO 130 J=1,NP
        TEMP = TH(J)
        P(J)=DIFZ(J)*TH(J)
        TH(J)= TH(J)+P(J)
        Q(J)=0
        JS = JS + NOB
        DO 102 I=1,NFIX
            IF(IVARY(I).EQ.1) VAL(I)=TH(IPOINT(I))
102  CONTINUE
        CALL MODEL(NPROB, TH, DELZ(JS), NOB, NP)
        IJ = JS-1
        DO 120 I = 1, NOB
            IJ = IJ + 1
            DELZ(IJ) = DELZ(IJ) - F(I)
120  Q(J) = Q(J) + DELZ(IJ) * R(I)
        Q(J)= Q(J)/P(J)
C          Q=XT*R (STEEPEST DESCENT)
130 TH(J) = TEMP
    GO TO LAOS,(131,414)
131 DO 150 I = 1, NP
    DO 151 J=1,I
        SUM = 0
        KJ = NOB*(J-1)
        KI = NOB*(I-1)
        DO 160 K = 1, NOB
            KI = KI + 1
            KJ = KJ + 1
160  SUM = SUM + DELZ(KI) * DELZ(KJ)
        TEMP= SUM/(P(I)*P(J))
        JI = J + NP*(I-1)
        D(JI) = TEMP
        IJ = I + NP*(J-1)
151 D(IJ) = TEMP
150 E(I) = SQRT(D(JI))
666 CONTINUE
    DO 153 I = 1, NP
        IJ = I-NP
        DO 153 J=1,I
            IJ = IJ + NP
            A(IJ) = D(IJ) / (E(I)*E(J))
            JI = J + NP*(I-1)

```

```

153 A(JI) = A(IJ)
C          A= SCALED MOMENT MATRIX
      II = - NP
      DO 155 I=1,NP
      P(I)=Q(I)/E(I)
      PHI(I)=P(I)
      II = NP + 1 + II
155 A(II) = A(II) + GA
      I=1
      CALL MATIN(A, NP, P, I, DET)
C          P/E = CORRECTION VECTOR
      STEP=1.0
      SUM1=0.
      SUM2=0.
      SUM3=0.
      DO 231 I=1,NP
      SUM1=P(I)*PHI(I)+SUM1
      SUM2=P(I)*P(I)+SUM2
      SUM3= PHI(I) * PHI(I) + SUM3
231 PHI(I) = P(I)
      TEMP = SUM1/SQRT(SUM2*SUM3)
      TEMP = AMIN1(TEMP, 1.0)
      TEMP = 57.295*ACOS(TEMP)
      WRITE(4, 1041) DET, TEMP
170 DO 220 I = 1, NP
      P(I) = PHI(I) *STEP / E(I)
      TB(I) = TH(I) + P(I)
220 CONTINUE
      WRITE(4, 7000)
7000 FORMAT(' TEST POINT PARAMETER VALUES')
      WRITE(4, 2006) (TB(I), I = 1, NP)
      DO 221 I = 1, NP
      IF(SIGNS(I)) 221, 221, 222
222 IF(SIGN(1.0,TH(I))*SIGN(1.0,TB(I))) 663, 221, 221
221 CONTINUE
      SUMB=0
      DO 223 I=1,NFIX
      IF(IVARY(I).EQ.1) VAL(I)=TB(IPOINT(I))
223 CONTINUE
      CALL MODEL(NPROB, TB, F, NOB, NP)
      DO 230 I=1,NOB
      R(I)=Y(I)-F(I)
230 SUMB=SUMB+R(I)*R(I)
      WRITE(4, 1043) SUMB
      WRITE(*,3002) SUMB,(VAL(I),I=1,NFIX)

```

```

WRITE(10,3002) SUMB,(VAL(I),I=1,NFIX)
3002 FORMAT(' ',1PE9.2,0P7E12.5)
WRITE(4, 1011)
WRITE(4, 2006) (F(I),I=1,NOB)
IF(SUMB - (1.0+EPS1)*SSQ) 662, 662, 663
663 IF( AMIN1(TEMP-30.0, GA)) 665, 665, 664
665 STEP=STEP/2.0
INTCNT = INTCNT + 1
IF(INTCNT-MAXCNT) 170,2700,2700
664 GA=GA*FNU
INTCNT = INTCNT + 1
IF(INTCNT-MAXCNT) 666,2700,2700
662 WRITE(4, 1007)
DO 669 I=1,NP
669 TH(I)=TB(I)
CALL GASS60(1, NP, TH, TEMP, TEMP)
WRITE(4, 1040) GA, SUMB
GO TO IRAN,(225,270,265)
225 DO 240 I = 1, NP
IF(ABS(P(I))/(1.E-20+ABS(TH(I)))-EPS2) 240, 240, 241
241 GO TO JORDAN,(265,270)
240 CONTINUE
WRITE(4, 1009) EPS2
GO TO 280
265 IF(ABS(SUMB - SSQ) - EPS1*SSQ) 266, 266, 270
266 WRITE(4, 1010) EPS1
GO TO 280
270 SSQ=SUMB
NIT=NIT+1
IF(NIT - MIT) 100, 100, 280
2700 WRITE(4, 2710)
2710 FORMAT(/115H **** THE SUM OF SQUARES CANNOT BE REDUCED TO
THE SUM
10F SQUARES AT THE END OF THE LAST ITERATION - ITERATING STOPS
/)
C
END ITERATION
280 WRITE(4, 1011)
WRITE(4, 2001) (F(I), I = 1, NOB)
WRITE(4, 1012)
WRITE(4, 2001) (R(I), I = 1, NOB)
SSQ=SUMB
IDF=NOB-NP
WRITE(4, 1015)
I=0
CALL MATIN(D, NP, P, I, DET)

```

```

DO 7692 I=1,NP
  II = I + NP*(I-1)
7692 E(I) = SQRT(D(II))
DO 340 I=1,NP
  JI = I + NP*(I-1) - 1
  IJ = I + NP*(I-2)
DO 340 J = I, NP
  JI = JI + 1
  A(JI) = D(JI) / (E(I)*E(J))
  IJ = IJ + NP
340  A(IJ) = A(JI)
      CALL GASS60(3, NP, TEMP, TEMP, A)
      WRITE(4, 1016)
      CALL GASS60(1, NP, E, TEMP, TEMP)
      IF(IDF) 341, 410, 341
341  SDEV = SSQ / IDF
      WRITE(4, 1014) SDEV, IDF
      SDEV = SQRT(SDEV)
      WRITE(4,3007) (PNAME(I),I=1,NFIX)
      WRITE(*,3007) (PNAME(I),I=1,NFIX)
      WRITE(10,3007) (PNAME(I),I=1,NFIX)
3007  FORMAT(/T6,'SSQ',T11,7A12)
      DO 3008 I=1,NFIX
      IF(IVARY(I).EQ.1) VAL(I)=TH(IPOINT(I))
3008  CONTINUE
      WRITE(*,3004) SSQ,(VAL(I),I=1,NFIX)
      WRITE(10,3004) SSQ,(VAL(I),I=1,NFIX)
      WRITE(4,3004) SSQ,(VAL(I),I=1,NFIX)
3004  FORMAT(1PE10.2,0P7E12.5)
      DO 3005 I=1,NP
3005  P(I)=E(I)*SDEV
      DO 3009 I=1,NFIX
      VAL(I)=0.0
      IF(IVARY(I).EQ.1) VAL(I)=P(IPOINT(I))
3009  CONTINUE
      WRITE(*,3006) (VAL(I),I=1,NFIX)
      WRITE(10,3006) (VAL(I),I=1,NFIX)
      WRITE(4,3006) (VAL(I),I=1,NFIX)
3006  FORMAT(' Std. Dev.',7E12.5)
      DO 391 I=1,NP
      P(I)=TH(I)+2.0*E(I)*SDEV
391  TB(I)=TH(I)-2.0*E(I)*SDEV
      WRITE(4, 1039)
      CALL GASS60(2, NP, TB, P, TEMP)
C returns with out confidence limits on function values

```

```

RETURN
ASSIGN 414 TO LAOS
GO TO 101
414 DO 415 K = 1, NOB
    TEMP = 0
    DO 420 I=1,NP
        DO 420 J=1,NP
            ISUB = K+NOB*(I-1)
            DEBUG1 = DELZ(ISUB)
            ISUB = K+NOB*(J-1)
            DEBUG2 = DELZ(ISUB)
            IJ = I + NP*(J-1)
            DEBUG3 = D(IJ)/(DIFZ(I)*TH(I)*DIFZ(J)*TH(J))
420    TEMP = TEMP + DEBUG1 * DEBUG2 * DEBUG3
        TEMP = 2.0*SQRT(TEMP)*SDEV
        R(K)=F(K)+TEMP
415    F(K)=F(K)-TEMP
        WRITE(4, 1008)
        IE=0
        DO 425 I=1,NOB,10
            IE=IE+10
            IF(NOB-IE) 430,435,435
430    IE=NOB
435    WRITE(4, 2001) (R(J), J = I, IE)
425    WRITE(4, 2006) (F(J), J = I, IE)
410    WRITE(4, 1033) NPROB
        RETURN
99    WRITE(4, 1034)
        GO TO 410
10000FORMAT(38H NON-LINEAR ESTIMATION, PROBLEM NUMBER I3,// I5,
1    14H OBSERVATIONS, I5, 11H PARAMETERS I14, 17H SCRATCH
REQUIRED)
1001 FORMAT(/25H INITIAL PARAMETER VALUES )
1002 FORMAT(/54H PROPORTIONS USED IN CALCULATING DIFFERENCE
QUOTIENTS )
1003 FORMAT(/25H INITIAL SUM OF SQUARES = E12.4)
1004 FORMAT(/////45X,13HITERATION NO. I4)
1007 FORMAT(/32H PARAMETER VALUES VIA REGRESSION )
1008 FORMAT(/////54H APPROXIMATE CONFIDENCE LIMITS FOR EACH
FUNCTION VAL
1UE )
10090FORMAT(/62H ITERATION STOPS - RELATIVE CHANGE IN EACH
PARAMETER LE
1SS THAN E12.4)

```

```

10100FORMAT(/62H ITERATION STOPS - RELATIVE CHANGE IN SUM OF
SQUARES LE
      1SS THAN  E12.4)
1011 FORMAT(22H0   FUNCTION VALUES )
1012 FORMAT(////10H RESIDUALS )
1014 FORMAT(//24H VARIANCE OF RESIDUALS =  ,E12.4,1H,I4,
      120H DEGREES OF FREEDOM )
1015 FORMAT(////19H CORRELATION MATRIX )
1016 FORMAT(////21H NORMALIZING ELEMENTS )
1033 FORMAT(/19H END OF PROBLEM NO. I3)
1034 FORMAT(/16H PARAMETER ERROR )
10390FORMAT(/71H INDIVIDUAL CONFIDENCE LIMITS FOR EACH
PARAMETER (ON LI
      1NEAR HYPOTHESIS) )
10400FORMAT(/9H LAMBDA =E10.3,40X,33HSUM OF SQUARES AFTER
REGRESSION =
      1E15.7)
1041 FORMAT(14H DETERMINANT =  E12.4, 6X, 25H ANGLE IN SCALED
COORD. =
      1 F5.2, 8HDEGREES )
1043 FORMAT(28H TEST POINT SUM OF SQUARES =  E12.4)
2001 FORMAT(/10E12.4)
2006 FORMAT(10E12.4)
      END
      SUBROUTINE MATIN(A, NVAR, B, NB, DET)
      DIMENSION A(NVAR, 1), B(NVAR, 1)
      PIVOTM = A(1,1)
      DET = 1.0
      DO 550 ICOL = 1, NVAR
      PIVOT = A(ICOL, ICOL)
      PIVOTM = AMIN1(PIVOT, PIVOTM)
      DET = PIVOT * DET
C   DIVIDE PIVOT ROW BY PIVOT ELEMENT
      A(ICOL, ICOL) = 1.0
      PIVOT = AMAX1(PIVOT, 1.E-20)
      PIVOT = A(ICOL, ICOL)/PIVOT
      DO 350 L=1,NVAR
350  A(ICOL, L) = A(ICOL, L)*PIVOT
      IF(NB .EQ. 0) GO TO 371
      DO 370 L=1,NB
370  B(ICOL, L) = B(ICOL, L)*PIVOT
C   REDUCE NON-PIVOT ROWS
371  DO 550 L1=1,NVAR
      IF(L1 .EQ. ICOL) GO TO 550
      T = A(L1, ICOL)

```



```

      A(L1, ICOL) = 0.
      DO 450 L=1,NVAR
450   A(L1, L) = A(L1, L) - A(ICOL, L)*T
      IF(NB .EQ. 0) GO TO 550
      DO 500 L=1,NB
500   B(L1, L) = B(L1, L)-B(ICOL,L)*T
550   CONTINUE
      RETURN
      END
      SUBROUTINE GASS60(ITYPE, NQ, A, B, C)
      DIMENSION A(NQ),B(NQ),C(NQ,NQ)
      NP = NQ
      NR = NP/10
      LOW = 1
      LUP = 10
10    IF( NR )15,20,30
15    RETURN
20    LUP=NP
      IF(LOW .GT. LUP) RETURN
30    WRITE(4, 500) (J,J=LOW,LUP)
      GO TO (40,60,80),ITYPE
40    WRITE(4, 600) (A(J),J=LOW,LUP)
      GO TO 100
60    WRITE(4, 600) (B(J),J=LOW,LUP)
      GO TO 40
80    DO 90 I=LOW,LUP
90    WRITE(4, 720) I,(C(J,I),J=LOW,I)
      LOW2=LUP+1
      IF(LOW2 .GT. NP) GO TO 100
      DO 95 I=LOW2,NP
95    WRITE(4, 720) I,(C(J,I),J=LOW,LUP)
100   LOW = LOW + 10
      LUP = LUP + 10
      NR = NR - 1
      GO TO 10
500   FORMAT(/I8,9I12)
600   FORMAT(10E12.4)
720   FORMAT(1H0,I3,1X,F7.4,9F12.4)
1     CONTINUE
      RETURN
      END
C THE MODEL

```

File Name: Batchm.for

SUBROUTINE MODEL (NPROB,P,F,NOB,NP)

C IMPLICIT NONE

C

C

Batch model for use with fitting routine TESTFIT

c

c

Set up to handle multiple experiments (10)

c

C

C

DOUBLE PRECISION RKD,DEFF,DPATH,RLAM,XSS0,FAST

DOUBLE PRECISION XM(10),V(10),PC0(10),XEFT(10),TF

DOUBLE PRECISION TBCC(220),VR(220),VA(220),CA(220)

DOUBLE PRECISION XMR,XKPR,XKR,XFR,XSR0

DOUBLE PRECISION X(250)

DOUBLE PRECISION ANS(0:500001),TIME,CTIME,STOLD,RSLOW

DOUBLE PRECISION XIC(501),DELTA(501),FN(501),CL,VS

DIMENSION IX(250),NEFD(10)

INTEGER FDOMAIN

CDLC

C Ed I'm confused here about how to pass P and F to

C the fitting program. I copied the following dimension

C statement from the old code, but I don't understand

CDLC

DIMENSION F(1),P(1)

C

CHARACTER*8 PNAME(7)

DIMENSION VAL(7),IPOINT(7),IVARY(7)

COMMON /BMOD/XM,V,PC0,XEFT,NEFD,TBCC,VR,VA,CA

COMMON /BMODA/XMR,XKPR,XKR,XFR,IFLAG,TF

COMMON /VALUE/ VAL,IPOINT,IVARY,PNAME,NFIX

COMMON /BDAT/ IX,X,NEXP

C

C READ DATA FROM PARAMETERS

RKD=VAL(1)

DPATH=VAL(3)

DEFF=VAL(2)

RLAM=VAL(4)

XSS0=VAL(5)

FAST=VAL(6)

C

C ED: RKD IS THE KD AND CL IS THE AQUEOUS CONC

C VR is the volume removed per sample, change

C this later to an array

```

C   VS is the current aqueous volume, modified as
C   samples are taken
C   VA is the volume added, CA is the conc of added
C   liquid.
c
C   NFRAC is the number of compartments
c
      NFRAC=(RLAM+2.d0)*10+1
      IF (NFRAC.LT.50) NFRAC=50
      IF (NFRAC.GT.500) WRITE(6,*) 'NFRAC = ', NFRAC
      IF (NFRAC.GT.500) WRITE(10,*) 'NFRAC = ', NFRAC
      IF (NFRAC.GT.500) WRITE(4,*) 'NFRAC = ', NFRAC
C
C
C   Loop through each experiment and set up appropriate
C   initial conditions
C
      NSUM=0
      IT=1
      DO 200 IEXP=1,NEXP
C
      CL=(PC0(IEXP)*V(IEXP)+XM(IEXP)*XSS0*FAST)/
      (V(IEXP)+RKD*XM(IEXP)*FAST)
      VS=V(IEXP)
C
C   Input the domain partitioning. Delta(I) is the delta for
C   each compartment.
C
      DO 10 I=1,NFRAC
        DELTA(I)=DPATH/NFRAC
10    CONTINUE
C
C   Subroutine INTF generates the F(i)'s by integrating f(delta)
C   with RLAM as the shape parameter
C
C
C   Set the initial condition within the immobile zone
C
C
      CALL INTF(RLAM,DELTA,DPATH,NFRAC,FN)
C
C   STOLD is the sum of the S for the diffusion compartments
C
      STOLD=0.0
      DO 20 I=1,NFRAC

```

```

      XIC(I)=XSS0*FN(I)*(1.D0-FAST)
      STOLD=STOLD+XIC(I)
20  CONTINUE
C
C   Loop through each flow domain
C
      FDOMAIN=1
      TIME=0.0
C   Note the the final time is X(NOBS)
      DO WHILE (FDOMAIN.LE.(NEFD(IEXP)+1))
C
C           Calculate ANS for beginning of boundary condition
C
      IF (IFLAG.EQ.1) THEN
        ANS(0)=CL
      ELSE
        ANS(0)=(STOLD+FAST*RKD*CL)/CL
      END IF
C
C
C   CTIME is the cumulative solution time
      CTIME=TBCC(FDOMAIN+NSUM)
      IF (FDOMAIN.EQ.(NEFD(IEXP)+1)) THEN
        DO 210 JCOUNT=1,NOB
          IF (IX(JCOUNT).EQ.IEXP) CTIME=X(JCOUNT)
210    CONTINUE
        END IF
C
C
C           Calculate retardation factor for slow sites
C
      RSLOW=(XM(IEXP)*RKD*(1.d0-FAST))/VS
C
C           calculate the number of time steps for the BC
C
      ITHALF=(CTIME-
TIME)*RSLOW*FN(1)*DEFF/(TF*DELTA(1)**2.d0)+1
      ITSTEPS=ITHALF*2
C
C           set minimum value of ITSTEPS
C
      IF (ITSTEPS.LT.100) GOTO 30
      GOTO 35

```

```

30      IF ((CTIME-TIME).GT.(XEFT(IEXP)/200.d0)) ITSTEPS=100
c      IF ((ITSTEPS.LT.100).AND.((CTIME-TIME).GT.(XEFT(IEXP)/
c          200.d0))) ITSTEPS=100
c
c      warn if number of time steps exceeds array size
c
35  CONTINUE
      IF (ITSTEPS.GT.500000) WRITE(6,*) 'ITSTEPS = ', ITSTEPS
      IF (ITSTEPS.GT.500000) WRITE(10,*) 'ITSTEPS = ', ITSTEPS
      IF (ITSTEPS.GT.500000) WRITE(4,*) 'ITSTEPS = ', ITSTEPS
      IF (ITSTEPS.GT.500000) GOTO 2222
c
c
C      FDSOLVE computes the soln from time to ctime for itsteps and
C      passes the soln back as array ANS(ITSTEPS)
c
      CALL FDSOLVE(TIME,CTIME,ITSTEPS,ANS,XIC,
      FN,DELTA,CL,STOLD,VS,IEXP,NFRAC)
C
C      INTERP interpolates the soln from FDSOLVE onto the observation
C      times and stores the results in array F(nobs)
C
      DO WHILE ((X(IT).LE.CTIME).AND.(X(IT).GE.TIME)
      .AND.(IX(IT).EQ.IEXP))
      CALL INTERP(X(IT),TIME,CTIME,ANS,ITSTEPS,F(IT))
      IT=IT+1
      END DO
      TIME=CTIME
C
C      Adjust aqueous volume and new aqueous conc.
C
C
C
C
      RFASTV=XM(IEXP)*RKD*FAST+VS
      XMADD=VA(FDOMAIN+NSUM)*CA(FDOMAIN+NSUM)
      XMREM=VR(FDOMAIN+NSUM)*CL
      XNEWM=RFASTV*CL+XMADD-XMREM
      CL=XNEWM/(RFASTV-VR(FDOMAIN+NSUM)+VA(FDOMAIN+NSUM))
c      CL=(VS*CL+VA(FDOMAIN+NSUM)*CA(FDOMAIN+NSUM)-
c          VR(FDOMAIN+NSUM)*CL)/
c          (VS-VR(FDOMAIN+NSUM)+VA(FDOMAIN+NSUM))
      VS=VS-VR(FDOMAIN+NSUM)+VA(FDOMAIN+NSUM)
      FDOMAIN=FDOMAIN+1
C

```

```
        END DO
        NSUM=NSUM+NEFD(IEXP)
200    CONTINUE
C
C    Output the results
C
CDLC    I=1
CDLC    DO WHILE (I.LT.NOB)
CDLC        WRITE(*,*)I,F(I)
CDLC        I=I+1
CDLC    END DO
CDLC    STOP
2222 CONTINUE
        RETURN
        END
```

File Name: Fdsolvem.for

```
SUBROUTINE FDSOLVE(TIME,CTIME,ITSTEPS,ANS,XIC,
.FN,DELTA,CL,STOLD,VS,IEXP,NFRAC)
C
C   IMPLICIT NONE
      DOUBLE PRECISION RKD,DEFF,DPATH,RLAM,XSS0,FAST
      DOUBLE PRECISION XM(10),V(10),PC0(10),XEFT(10),TF
      DOUBLE PRECISION TBCC(220),VR(220),VA(220),CA(220)
      DOUBLE PRECISION XMR,XKPR,XKR,XFR,XSR0
      DOUBLE PRECISION ANS(0:500001),TIME,CTIME,STOLD,RSLOW
      DOUBLE PRECISION XIC(501),DELTA(501),FN(501),CL,VS
      DOUBLE PRECISION K(501),RES(501),A(501),B(501),RESN,ANS2
      INTEGER ITSTEPS,NFRAC
      DOUBLE PRECISION SNEW(501),SOLD(501),ST,DELTAT
      DIMENSION IFC(220),NEFD(10)
      CHARACTER*8 PNAME(7)
      DIMENSION VAL(7),IPOINT(7),IVARY(7)
      COMMON /BMOD/XM,V,PC0,XEFT,NEFD,TBCC,VR,VA,CA
      COMMON /BMODA/XMR,XKPR,XKR,XFR,IFLAG,TF
      COMMON /VALUE/ VAL,IPOINT,IVARY,PNAME,NFIX
C
C   DELTAT=(CTIME-TIME)/ITSTEPS
C
C   This version of FDSOLVE solves the compartment
C   equations using backward Euler time differencing
C   to avoid stability problems. The first-order
C   accuracy should be OK since it matches the first-order
C   spatial accuracy
C
C   Note a Gauss-Seidel solver is used to solve the
C   tridiagonal matrix system that results from the
C   Backward Euler application
C
C       This version of fdsolvem set up for:
C           BATCH systems
C           Fitting multiple experiments
C
C   Set initial conditions from XIC input
C   Also use this for initial guess for Gauss-Seidel solver
C
      RKD=VAL(1)
      DEFF=VAL(2)
      DPATH=VAL(3)
      RLAM=VAL(4)
```

```

XSS0=VAL(5)
FAST=VAL(6)
DO 10 I=1,NFRAC
  SOLD(I)=XIC(I)
  SNEW(I)=XIC(I)
10 CONTINUE
C
  NCOUNT=1
C
C
C  Set up constant used to avoid extra calculations
C  see Dave's notes
  K(1)=2.0*DEFF*DELTAT/(DELTA(1)**2)
  DO 20 J=2,NFRAC
    K(J)=2.0*DEFF*DELTAT/((DELTA(J-1)+DELTA(J))*DELTA(J))
20 CONTINUE
C
C  Set up matrix constants
  DO 30 J=1,NFRAC-1
C    Diagonal term
    A(J)=1.0+K(J)+FN(J+1)*K(J+1)/FN(J)
30 CONTINUE
C
  A(NFRAC)=1.0+K(NFRAC)
  DO 40 J=2,NFRAC
C    Subdiagonal term
    B(J)=-K(J)*FN(J)/FN(J-1)
40 CONTINUE
C  Note that the super diagonal term is just
C  equal to -k(j), j=1,nfrac-1
C
  DO WHILE (NCOUNT.LE.ITSTEPS)
C
C    Gauss-Seidel iteration
    IGITER=0
    RESN=1.0
    DO WHILE((RESN.GT.0.00001).AND.(IGITER.LT.50))
C
      SNEW(1)=(K(2)*SNEW(2)+SOLD(1)+K(1)*FN(1)
        *RKD*(1.D0-FAST)*CL)/A(1)
C
      DO 50 J=2,NFRAC-1
        SNEW(J)=(SOLD(J)+K(J+1)*SNEW(J+1)-B(J)*SNEW(J-1))/A(J)
C

```



```

50    CONTINUE
      SNEW(NFRAC)=(SOLD(NFRAC)-B(NFRAC)*SNEW(NFRAC-
1)))/A(NFRAC)
C
C      compute residual
C
      RESN=0.0
      RES(1)=A(1)*SNEW(1)-K(2)*SNEW(2)-
      SOLD(1)-K(1)*FN(1)*RKD*CL*(1.D0-FAST)
C
      RESN=RESN+(RES(1))**2
C
      DO 60 J=2,NFRAC-1
C
        RES(J)=A(J)*SNEW(J)-K(J+1)*SNEW(J+1)+
        B(J)*SNEW(J-1)-SOLD(J)
        RESN=RESN+(RES(J)**2)
60    CONTINUE
C
      RES(NFRAC)=A(NFRAC)*SNEW(NFRAC)+
      B(NFRAC)*SNEW(NFRAC-1)-SOLD(NFRAC)
      RESN=RESN+(RES(NFRAC)**2)
      RESN=SQRT(RESN)
      IITER=IITER+1
C
C      End Gauss-Seidel loop
C
      END DO
C
      Add the sorbed concentrations to update cl
C
      ST=SNEW(1)
      DO 70 J=2,NFRAC
        ST=ST+SNEW(J)
70    CONTINUE
C
C      Update the aqueous concentration using the
C      sorbed concentration solutions
C
      CL=CL+(XM(IEXP)/(VS+RKD*FAST*XM(IEXP)))*(STOLD-ST)
      ANS(NCOUNT)=CL
      ANS2=(ST+FAST*RKD*CL)/CL
      IF (IFLAG.EQ.0) ANS(NCOUNT)=ANS2
C
      DO 80 I=1,NFRAC

```

```
        SOLD(I)=SNEW(I)
        XIC(I)=SNEW(I)
80      CONTINUE
C
        STOLD=ST
        NCOUNT=NCOUNT+1
END DO
RETURN
END
```

File Name: Intf.for

SUBROUTINE INTF(RLAM,DELTA,DMAX,NFRAC,FN)

DOUBLE PRECISION DELTA(501),FN(501),RLAM,DMAX

INTEGER NFRAC

FAC=(RLAM+1)/(DMAX**(RLAM+1))

I=1

X=0.0

DO WHILE (I.LT.NFRAC)

C Apply Simpson's rule

C FN(I)=DELTA(I)*FAC/6.0*((DMAX-X)**RLAM+

C .4.0*(DMAX-(X+DELTA(I)/2))**RLAM+

C .(DMAX-(X+DELTA(I)))**RLAM)

FN(I)=(((DMAX-X)**(RLAM+1.D0))-(DMAX-(X+DELTA(I)))**

. (RLAM+1.D0))/(DMAX**(RLAM+1.D0))

X=X+DELTA(I)

I=I+1

END DO

C FN(NFRAC)=FAC*DELTA(NFRAC)

FN(NFRAC)=(DELTA(NFRAC)**(RLAM+1.D0))/(DMAX**(RLAM+1.D0))

RETURN

END

File Name: Interp.for

SUBROUTINE INTERP(XT,TIME,CTIME,ANS,ITSTEPS,FR)

DOUBLE PRECISION ANS(0:500001),TIME,CTIME,XT,DELTAT

DOUBLE PRECISION TIMEC

INTEGER ITSTEPS

C

DELTAT=(CTIME-TIME)/ITSTEPS

NCOUNT=0

TIMEC=TIME

DO WHILE (XT.GT.TIMEC)

TIMEC=TIMEC+DELTAT

NCOUNT=NCOUNT+1

END DO

C FR=(ANS(NCOUNT)+ANS(NCOUNT-1))/2.D0

FR=(ANS(NCOUNT)-ANS(NCOUNT-1))*(XT-TIMEC+DELTAT)

./DELTAT+ANS(NCOUNT-1)

IF (XT.EQ.TIME) FR=ANS(0)

IF (XT.EQ.CTIME) FR=ANS(ITSTEPS)

RETURN

END

REFERENCES

- Augustijn, D. C. M. (1993)
Chemodynamics of Complex Waste Mixtures: Applications to Contamination and Remediation of Soils and Aquifer Media, Ph.D. Dissertation, University of Florida, Gainesville.
- Ball, W. P. and Roberts, P. V. (1991)
"Long-term Sorption of Halogenated Organic Chemicals by Aquifer Material and Intraparticle Diffusion," Environmental Science and Technology, 25 : 1236-1249
- Barber, L. B., Thurman, E. M., and Runnells, D. D. (1992)
"Geochemical Heterogeneity in A Sand and Gravel Aquifer: Effects of Sediment Mineralogy and Particle Size on the Sorption of Chlorobenzenes," Journal of Contaminant Hydrology, 9 : 35-54.
- Bowman, B. T. (1979)
"Method for Repeated Additions for Generating Pesticide Adsorption-Desorption Isotherm Data," Canadian Journal of Soil Science, 59 : 435-437.
- Brusseau, M. L., Jessup, R. E., and Rao, P.S.C. (1991)
"Nonequilibrium Sorption of Organic Chemicals: Elucidation of Rate-Limiting Processes," Environmental Science and Technology, 25 : 134-142.
- Brusseau, M. L., Jessup, R. E., Rao, P.S.C., and Davidson, J. M. (1989)
"Flow Interruption: A Method for Investigating Sorption Nonequilibrium," Journal of Contaminant Hydrology, 4 : 223-240.
- Brusseau, M. L., and Rao, P.S.C. (1989a)
"Sorption Nonideality During Organic Contaminant Transport in Porous Media," CRC Critical Review in Environmental Control, 19 : 33-99.
- Brusseau, M. L., and Rao, P.S.C. (1989b)
"The Influence of Sorbate-Organic Matter Interactions on Sorption Nonequilibrium," Chemosphere, 18(9) : 1691-1706
- deVenoge, T. P. (1996)
Development of Synthetic Soils for Sorption Mass Transfer Model Validation, M. S. Thesis, Air Force Institute of Technology, Wright-Patterson AFB, OH.
- Di Toro, D. M. and Horzempa, L. M., (1982)
"Reversible and Resistant Components of PCB Adsorption-Desorption Isotherm," Environmental Science and Technology, 16(9) : 594-602

- Harmon, T. C., Semprini, L., and Roberts, P. V. (1992)
"Simulating Solute Transport Using Laboratory-based Sorption Parameters,"
Journal of Environmental Engineering, 118 : 666-689.
- Heyse, E. (1994)
Mass Transfer Between Organic and Aqueous Phases: Investigation Using a Continuously Stirred Flow Cell, Ph.D. Dissertation, University of Florida, Gainesville.
- Karickhoff, S.W. and Morris, K. W. (1985)
"Sorption Dynamics of Hydrophobic Pollutants in Sediment Suspensions,"
Environmental Toxicology and Chemistry, 4 : 469-479
- Lion, L. W., Stauffer, T. B., and MacIntyre, W. G. (1990)
"Sorption of Hydrophobic Pollutants in Sediment Suspensions," Journal of Contaminant Hydrology, 5 : 215-234.
- Mika, K. K. (1996)
Investigation of Sorption Mass Transfer Models Using Synthetic Soils, M.S. Thesis, Air Force Institute of Technology, Wright-Patterson AFB, OH.
- Nkedi-Kizza, P., Brusseau, M. L., Rao, P. S. C., and Hornsby, A. G. (1989)
"Nonequilibrium Sorption During Displacement of Hydrophobic Organic Chemicals and ⁴⁵Ca Through Soil Columns With Aqueous and Mixed Solvents,"
Environmental Science and Technology, 23 : 814-820.
- Pavlostathis, S. G., and Jaglal, K. (1991)
"Desorptive Behavior of Trichloroethylene in Contaminated Soil," Environmental Science and Technology, 25 : 274-279.
- Pedit, J. A. and Miller, C. T. (1994)
"Heterogeneous Sorption Processes in Subsurface Systems. 1. Model Formulations and Applications," Environmental Science and Technology, 28 : 2094-2104.
- Pignatello, J. J. (1990)
"Slowly Reversible Sorption of Aliphatic Halocarbons in Soils," Environmental Toxicology and Chemistry, 9 : 1117-1126.
- Pignatello, J. J., and Xing, B. (1996)
"Mechanisms of Slow Sorption of Organic Chemicals to Natural Particles,"
Environmental Science and Technology, 30(1) : 1-11

- Rao, P. S. C., Jessup, R. E., Davidson, J. M. (1980)
 "Experimental and Mathematical Description of Nonadsorbed Solute Transfer by Diffusion in Spherical Aggregates," Soil Science Society of America Journal, 44 : 684-688.
- Rebhum, M., Manka, J., and Rav-Acha, Ch. (1992)
 "Sorption of Organics on Clay and Synthetic Humic-Clay Complexes Simulating Aquifer Processes," Water Research, 26 : 79-84.
- Schnitzer, M. (1978)
 "Humic Substances: Chemistry and Reactions", In: Soil Organic Matter, (M. Schnitzer and S.U. Khan, Editors), Elsevier Scientific Publishing Company, Amsterdam :1-64.
- Scow, K. M., and Alexander, M. (1992)
 "Experimental Results With Synthetic Aggregates," Soil Science Society of America Journal, 56 : 128-134
- Weber, W. J., Yu, H., and Huang, W. (1996)
 "Hysteresis in the Sorption and Desorption of Hydrophobic Organic Contaminants by Soils and Sediment," Water Resources Research, Submitted: 16 Sep 1996.
- Weber, W. J. and Miller, C. T. (1988)
 "Modeling Sorption of Hydrophobic Contaminants by Aquifer Material," Water Resources Research 22 : 457-464.
- Wu, S. and Gschwend, P. M. (1986)
 "Sorption Kinetics of Hydrophobic Compounds to Natural Sediments and Soils," Environmental Science and Technology, 20 : 717-725.

VITA

Lt. Col. Kung-Fu Hwang [REDACTED]

[REDACTED] He grew up and attended schools in the same city until his graduation from Hou-Peng Junior High. In August 1976, he started his military life with a permission to enroll in the Chinese Air Force Youth School, which had the same education as the general senior high school, but trained cadets with military doctrine in daily life. Following his graduation in August 1978, he was permitted to become a cadet in the Academy of the Chinese Air Force. He graduated with a Bachelor of Science degree in Civil Engineering and was commissioned as a First Lieutenant in the Chinese Air Force in November 1982. He started his first duty assignment as a mechanical engineer on Chin-Chung-Kung Air Force Base (AFB) in Taichung County. Four years later in August 1986, he was assigned to the headquarters (HQ), working on the intelligence staff and stationed in Taipei City. In June 1988, he was transferred to work as a history officer on the headquarters staffs. Since September 1994, he worked as an English translator until his departure in January 1995 to pursue a Master of Science degree in Environmental Management and Engineering at the Air Force Institute of Technology, Wright-Patterson AFB, Ohio, United States of America. He is married to a wonderful wife, Hsiu-Fen Shih, and is the proud father of two beautiful and promising children: Lan, and Hao, [REDACTED]

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 074-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of the collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE June 1997		3. REPORT TYPE AND DATES COVERED Master's Thesis
4. TITLE AND SUBTITLE Study of Desorption of Contaminant from Synthetic Soil			5. FUNDING NUMBERS	
6. AUTHOR(S) Kung-Fu Hwang, Lt. Col., ROCAF				
7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(S) Air Force Institute of Technology 2950 P Street, Building 640 WPAFB OH 45433-6583			8. PERFORMING ORGANIZATION REPORT NUMBER AFIT/GEE/ENV/96D-08	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Office of Scientific Research (AFOSR)/NA ATTN: Capt Mike Chipley Bolling AFB, Washington D.C.			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (<i>Maximum 200 Words</i>) A better understanding of sorption and desorption processes could improve estimates of time and cost required for remedial activities, exposure times and health risk, and bioavailability. Conventional rate-limited sorption models do not accurately define the diffusion domain at the grain scale. Heyse (1994) proposed the multiple sites in series (MSS) model, which allows more general description of the geometry of the sorption domain than the classical spherical or discrete distributions. A version of this model was tested by deVenoge (1996). The model was able to accurately simulate sorption rate data, but could not estimate unique geometry parameters. This research is to develop techniques to study desorption, and compare the results to the sorption study conducted by deVenoge (1996). This study examines whether sorption and desorption of anthracene by paraffin are reversible processes. The ability of the MSS model to predict geometry parameters was also tested. One finding of this study was the apparent volatilization of anthracene from wax during the heating and molding processes. This phenomenon may be responsible for the non-zero intercept of the desorption isotherm. It may have also confounded the initial conditions required by the MSS model in predicting the sorption distribution. If the initial concentration of anthracene in the wax is adjusted, the desorption process does appear to be the reverse of the sorption process. The equilibrium partition coefficients for sorption and desorption are similar. The diffusion coefficient appears to be faster for desorption than sorption, but this may have been affected by solvation of the paraffin. The MSS model did not successfully predict geometry parameters, possibly due to uncertain initial concentration in wax.				
14. Subject Terms sorption, desorption, rate-limited, nonequilibrium process, diffusion model, mass transfer, partition coefficient, synthetic soil, batch experiment			15. NUMBER OF PAGES 110	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	